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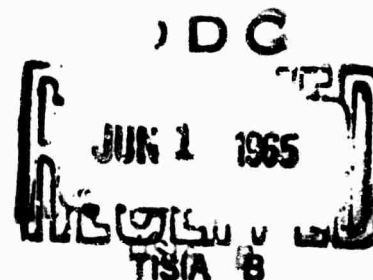
**FINAL REPORT**  
**FOR**  
**GROWTH OF BROAD LINEWIDTH RUBY CRYSTALS**

1 May 1962 to 30 April 1964  
NONR-3832(00), Amendment No. 1

Submitted by:  
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## I. PURPOSE

Our primary objective was to broaden the linewidth of ruby without disturbing its optical quality significantly, by placing  $\text{Cr}^{3+}$  in dilute solid solutions of  $\text{Al}_2\text{O}_3$  and  $\text{Ga}_2\text{O}_3$  and/or  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$ . Since the fluorescent transition in ruby is so strongly dependent on crystal field, it was felt that a very modest impurity concentration should be sufficient to broaden the linewidth. We planned to grow a two inch long, very narrow linewidth, low strain ruby by growth from a molten salt. Then, we planned to grow by the same method crystals of  $\text{Al}_2\text{O}_3$ - $\text{Ga}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ - $\text{Y}_2\text{O}_3$  activated with  $\text{Cr}^{3+}$ , in order to give us broad linewidth  $\text{Cr}^{3+}$  fluorescence with little or no change in the optical quality of the host crystal.

## II. ABSTRACT

Progress has been achieved in perfecting the techniques for the growth of ruby from flux and broadening the fluorescent linewidth by Ga additions. It has been demonstrated that large flux free ruby crystals suitable for fabrication into laser rods can be produced by spontaneous nucleation from slowly cooled molten salts.

By lowering the pedestal supporting an 8 inch x 8 inch crucible until a 200°C gradient is obtained, and slowly cooling a  $\text{PbF}_2$  melt at 1.5°C per hour, large ruby plates up to 3/8 inches thick and 2 inches in maximum dimensions have been grown. Attempts to grow larger crystals by growth on ruby seeds were not successful, but it was established that crystals can be grown free from chromium content variation by using ruby nutrient and growing crystals in a temperature gradient under steady state conditions.

Solubility of  $\text{Al}_2\text{O}_3$  in  $\text{PbF}_2$  has been measured and the effect of Cr and Ga on the solubility has been determined. Chemical analysis of the crystals shows a concentration gradient exists for Cr but not for Ga.

Line broadening was achieved in ruby crystals both by the deliberate addition of Ga, and by the substitution of  $\text{O}^{2-}$  by  $\text{F}^-$  during crystal growth. Broadening in excess of  $10 \text{ cm}^{-1}$  was obtained due to a combination of these factors.

Two rods cut from these crystals lased at 2000 and 1200 joules respectively in a 3 inch long laser head at 200°K.

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## V. STATUS

A number of goals were established during the course of this contract. Table I shows the present status of these goals.

The primary goal of the contract, the growth of ruby from flux and the addition of Ga, has been achieved. A method is described for the growth of large single crystals of high optical quality. A cooling rate of  $1.5^{\circ}\text{C}$  was used but further work on the effect of cooling rate is suggested.

White <sup>(1)</sup> has reported that high purity starting materials has led to a reduction in laser threshold. This effect was not determined by us but high purity  $\text{PbF}_2$  and  $\text{Al}_2\text{O}_3$  were used throughout the major portion of the contract.

The attempt to produce growth on a ruby seed, No. 77, was only partially successful and is discussed more fully in the section on crystal growth. It is felt that perhaps several additional runs would be needed to establish optimum conditions for this type of growth.



TABLE I

<u>Item</u>	<u>Goal</u>	<u>Purpose</u>	<u>Problems Encountered</u>
1	Study to determine growth conditions for Cr doped $Al_2O_3$	To provide crystals for evaluation	$Cr^{3+}$ distribution, Pt corrosion, included impurities
2	Determination of analytical procedures for the detection of Cr in $Al_2O_3$	Determination of Cr concentration in ruby crystals and flux	None
3	Determination of growth conditions for large, single crystals of ruby	Provide large ruby crystals for test purposes	Equipment failures, Pt corrosion, Cr concentration gradient
4	Determination of growth conditions for Ga doped ruby	Provide Ga doped crystals for test purposes	Equipment failures, Pt corrosion, Cr concentration
5	Determination of analytical procedures for the detection of Ga in $Al_2O_3$	Determination of Ga concentration in ruby crystals	Chemical separation
6	Determination of the effect of Ga impurity on the linewidth of ruby	Determine linewidth broadening	Equipment calibration
7	Comparison of the optical quality of narrow and broad linewidth ruby	Effect of line broadening on optical quality	Equipment calibration
8	Effect of large melts on crystal quality and size	Provide large ruby crystals for test purposes	Overflow of melt from crucible, rapid corrosion of Pt crucible

TABLE I (Continued)

<u>Item</u>	<u>Goal</u>	<u>Purpose</u>	<u>Problems Encountered</u>
9	Effect of crystallization temperatures and cooling rates on crystal quality and size	Improve crystal quality	Rapid deterioration of furnace and crucible at high temperatures
10	Effect of purity of $Al_2O_3$ and $PbF_2$ on crystal quality	Improve crystal quality	Maintain control of purity during run
11	Growth of ruby on seed crystals	Increase size of ruby and ruby in $PbF_2$ crystals	Restrict nucleation to seed
12	Determination of solubility of $Al_2O_3$ in $PbF_2$ and determine effect of Ga and Cr on the solubility	Draw solubility curve of $Al_2O_3$ , and show modification of system by Cr and Ga	Analytical techniques
13	Photograph light scatter from selected ruby crystals	Measure optical quality of crystals	Equipment acquisition
14	Determination of Cr, Ga, and Pb concentration by X-ray fluorescence	Provide a quick and reliable method of analysis	Equipment calibration

## VI. EXPERIMENTAL

A. Crystal Growth

A summary of all runs made during the contract is shown in Table II. Two methods of growth were attempted, spontaneous nucleation and growth on seeds.

1. Spontaneous Nucleation

We have succeeded in controlling ruby plate thickness by varying the temperature gradient during growth. In addition, we have demonstrated that thick plates can be grown as relatively flux free single crystals.

Crystals of ruby were initially precipitated (see Runs No. 2 and 7) from mixed  $\text{PbO-PbF}_2$  fluxes using a formula developed by Linares. (2) Using a 100 ml crucible, 0.2 m  $\text{Al}_2\text{O}_3$  was added to 200 grams of flux consisting of 120 grams  $\text{PbF}_2$  and 80 grams  $\text{PbO}$ .

From these 100 ml crucibles, and larger runs in 5 1/2 inch and then 8 inch cans, ruby crystallized as thin, heavily flux included, laminated plates, see Figure 1. A small portion of each run, however, contained what Linares referred to as a "rhombohedral phase", small crystals of high optical quality, well defined faces and no included flux. These crystals were usually found firmly attached to the wall or base of the Pt crucible, see Figure 2, as compared to the plates which were usually found on the surface of the melt.

In the Third Semiannual Report, a procedure was described for growth of ruby crystals from molten salt solutions. It has been observed, however, that only a small portion of this growth was in the form of thick

TABLE II

Run No.	Type of Run				Soak Temp.		Crucible Used	Purpose of Run	Soak Time, Hours	Cooling Rate, °C/hr.	Pour Temp., °C	Crystal Yield, gms	Yield, %	Rhombic, %	% Flux Loss	REMARKS
	Units	Al <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	CaO	Ph <sub>2</sub> O	°C										
1	gms moles m%	20.5 0.2 18.6	1.0 0.007 0.6	0.0 0.0 0.0	30.0 0.34 34.1	1275	100 ml crimped cover	Exploratory Crystal Growth	16	2.77	940	---	---	---	---	Incomplete solution.
2	Same as Run No. 1					1375	Same	Increased Solution	17	2.29	1080	15	73	---	30	Complete solution. Plates.
3	Two Times Run No. 1					---	Same	Fast preheating, pre-melting & stirring in order to increase yield.	17.5	2.29	1000	0.0	0.0	---	---	Furnace failure.
4	Same as Run No. 1					1370	Same	Reduce flux loss by better sealing of cover	17	2.25	980	---	---	---	4	Solidification of melt before flux could be poured.
5	gms moles m%	20.5 0.2 18.5	1.0 0.007 0.6	0.0 0.0 0.0	30.0 0.34 34.1	1280	Same	Effect on PbF <sub>2</sub> /PbO ratio on crystal habit	17	2.25	980	---	---	---	---	Incomplete solution.
6	Same as Run No. 1					---	Same	Higher temp. for solution	17	2.25	1100	21	100	---	48	Large crystal.
7	Three Times Run No. 1					1340	Same	Scale up 10 times (100 ml crucible, 1 1/4 inch can bit), preheated but not pre-melted	24 (stirring)	0.5	800	240	40	52	---	Controller failed but good yield. Pb can rendered useless by deep etching.
8	gms moles m%	672.5 6.4 20.5	1.5 0.02 0.06	0.0 0.0 0.0	1600.0 14.7 45.8	1100	Same	Reduced Cr content, 10% increase in Al <sub>2</sub> O <sub>3</sub> to give larger, more radiant. Higher soak temperature.	24 (stirring)	0.5	1050	310	46	4	17-25	Furnace failure, but satisfactory crystal yield.
9	gms moles m%	20.2 0.20 19.2	0.1 0.007 0.07	0.4 0.002 0.2	80.0 0.16 34.2	1460	100 ml crimped cover	Ga doped Ruby crystals	17	2.25	1090	---	---	0	39	Flux included plates.
10	gms moles m%	19.81 0.20 19.1	0.10 0.0007 0.07	0.04 0.004 0.4	80.0 0.34 34.2	1440	Same	Effect of Ga concentration on ruby crystals	17	2.25	1100	16.2	82	0	36	Flux included plates.
11	gms moles m%	19.17 0.19 18.1	0.1 0.0007 0.07	0.88 0.0007 0.95	80.0 0.34 34.2	1440	Same	Effect of Ga concentration on ruby crystals	17	2.25	1110	---	---	---	38	Flux included plates.
12-1	gms moles m%	22.55 0.22 18.8	0.05 0.0003 0.31	0.0 0.0 0.0	132.0 0.59 50.4	1440	Same	PbO/PbF <sub>2</sub> ratio on ruby crystal habit	95	5	1060	9.7	41	---	42	Timer failed to switch programmer, heavy flux inclusion.
12-1 (rerun)	gms moles m%	22.40 0.2 18.7	0.1 0.0007 0.06	0.0 0.0 0.0	120.0 0.54 50.4	1440	Same	Same	17	5	1160	7.2	35	13	---	Light flux included crystals solution and phase change.
12-2	gms moles m%	12.07 0.1 10.2	0.05 0.0003 0.03	0.0 0.0 0.0	80.0 0.54 55.9	1440	Same	Saturation on crystal growth	17	5	---	0	0	0	25	No yield.
12-3	gms moles m%	10.07 0.10 10.5	0.05 0.0001 0.03	0.0 0.0 0.0	80.00 0.16 37.9	1440	Same	PbO/PbF <sub>2</sub> & Al <sub>2</sub> O <sub>3</sub> concentration	17	5	900	6.1	40	---	49.8	Crystals of white shiny material indicating phase change.
12-4	gms moles m%	20.50 0.20 18.5	0.15 0.0007 0.06	0.6 0.0 0.0	160.00 0.72 56.8	1440	Same	Same	---	---	---	9	40	---	---	50 percent PbO, 50 white crystals.
12-5	gms moles m%	20.5 0.20 18.4	0.1 0.0007 0.06	0.0 0.0 0.0	160.0 0.81 71.5	1360	100 ml	PbO/PbF <sub>2</sub>	17	5	---	10.3	50	---	---	Possible incomplete solution.
13	gms moles m%	1035 10.2 18.8	10.15 0.06 0.11	0.0 0.0 0.0	4570 24.8 46.5	1280	5 1/4 inch can rotated	Crystal growth	24	0.5	1000	365.5	15.4	---	---	Cooling rate increased by accident. Possible incomplete solution but crystal quality excellent.
14	gms moles m%	820 8.1 19.1	8.20 0.05 0.11	0.0 0.0 0.0	1200 14.4 34.4	1280	5 1/4 inch can rotated	PbO/PbF <sub>2</sub> ratio on large crystals growth	24	0.5	1000	334.5	41	---	---	Heavily flux included plate.
14-1	gms moles m%	61.5 0.60 19.0	0.61 0.004 0.13	0.0 0.0 0.0	360 1.47 34.3	1340	250 ml garbage can type cover	Starting composition vs. % rh.	12	3.80	Solidified	15	25	Small amt.	6.5	Some crystal growth.
14-2	gms moles m%	61.50 0.60 19.0	0.61 0.004 0.13	0.0 0.0 0.0	100 1.22 42.5	Same	Same	Same	Same	Same	Same	---	---	---	3.8	Incomplete solution.
14-3	gms moles m%	61.50 0.60 18.4	0.61 0.004 0.12	0.0 0.0 0.0	160 1.62 40.4	Same	Same	Same	Same	Same	Same	---	---	---	7.3	Same.
21 (1-4)	gms moles m%	20.50 0.20 19.2	0.05 0.001 0.1	0.0 0.0 0.0	40.00 0.36 34.3	1290	100 ml	Isenthal growth	12	50	970 840 745	---	---	---	---	Incomplete solution in all cases but seed doubled in size.

$$\begin{array}{r} 2 \\ 4 \\ 6 \\ 8 \\ 10 \\ 12 \\ 14 \\ 16 \\ 18 \\ 20 \\ 22 \\ 24 \\ 26 \\ 28 \\ 30 \\ 32 \\ 34 \\ 36 \\ 38 \\ 40 \\ 42 \\ 44 \\ 46 \\ 48 \\ 50 \end{array}$$

Run No.	Units	Type of Run						Furnace Used	Crucible Used	Soak Temperature (°C)			Soak Time Hours	
		Al <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	Ga <sub>2</sub> O <sub>3</sub>	PbO	PbF <sub>2</sub>	Total			Purpose of Run	Ba	Pedestal		Plug
22 1-6	gms moles m %	20.50 0.20 18.9	0.20 0.0013 0.12	0 0 0	120.00 0.54 50.5	80.00 0.33 30.8	220.70 1.07 100.3	Repeat of No. 17, using 40 percent PbF <sub>2</sub>	Lindberg	100 ml	1290	---	---	12
23	gms moles m %	61.50 0.60 19.0	0.62 0.0041 0.13	0 0 0	360.00 1.61 50.5	240.00 0.98 30.7	662.12 3.19 100.3	Effect of stirring during cooling cycle.	10"	250 ml	1340	1280	---	4
24	gms moles m %	307.0 3.0 19.0	3.1 0.03 0.13	0 0 0	1800.0 4.7 50.5	1200.0 5.7 30.7	3310.0 17.43 100.3	Effect of deep melt on crystal growth	10"	12"	---	---	---	---
25-1	gms moles m %	30.75 0.30 27.0	0.31 0.002 0.20	0 0 0	0 0 0	200.00 0.82 73.2	231.06 1.12 100.4	Test feasibility of growth from 100 percent PbF <sub>2</sub>	10"	100 ml	---	1300	20	20
25-2	gms moles m %	41.70 0.40 32.8	0.41 0.0027 0.22	0 0 0	0 0 0	200.00 0.82 67.2	241.41 1.22 100.2	Same as No. 25-1	Same	Same	Same as No. 25-1			
25-3	gms moles m %	51.25 0.50 38.0	0.51 0.0034 0.26	0 0 0	0 0 0	200.00 0.82 62.0	251.76 1.34 100.3	Same as No. 25-1	Same	Same	Same as No. 25-1			
25-4	gms moles m %	82.00 0.80 49.0	0.82 0.0054 0.33	0 0 0	0 0 0	200.00 0.82 50.3	282.82 1.63 99.6	Same as No. 25-1	Same	Same	Same as No. 25-1			
26-1	gms moles m %	90.84 0.89 26.5	0.96 0.0063 0.19	1.68 0.009 0.27	0 0 0	600.00 2.45 73.0	693.48 3.36 100.0	Test feasibility of growth of Ga doped ruby from 100% PbF <sub>2</sub>	10"	50 ml	1330	1300	---	24
26-2	gms moles m %	87.46 0.86 25.6	0.96 0.0063 0.19	8.43 0.045 1.34	0 0 0	600.00 2.45 73.0	696.85 3.36 100.1	Same as No. 26-1	Same	Same	Same as No. 26-1			
26-3	gms moles m %	27.52 0.27 24.1	0.32 0.0021 0.18	5.62 0.030 2.68	0 0 0	200.00 0.82 73.2	233.46 1.12 10.2	Same as No. 26-1	10"	100 ml	Same as No. 26-1			
27	gms moles m %	820.00 8.04 33.0	8.20 0.034 0.22	0 0 0	0 0 0	4000.0 16.33 66.11	4828.20 24.42 100.0	Growth of Al <sub>2</sub> O <sub>3</sub> f. PbF <sub>2</sub>	10"	5 1/4"	---	1280	---	---
28-1	gms moles m %	90.84 0.89 26.5	0.48 0.0032 0.10	1.68 0.009 0.27	0 0 0	600.00 2.45 73.0	693.00 3.35 99.9	Growth of Ga doped ruby from PbF <sub>2</sub>	10"	250 ml	1380	1305	1360	24
28-2	gms moles m %	87.46 0.86 25.6	0.48 0.0032 0.10	8.43 0.045 1.34	0 0 0	600.00 2.45 73.0	696.57 3.36 99.9	Same as No. 28-1	Same	Same	Same as No. 28-1			
28-3	gms moles m %	28.14 0.28 25.0	0.16 0.0011 0.10	4.49 0.024 2.12	0 0 0	200.00 0.82 72.7	232.79 1.13 99.9	Same as No. 28-1	Same	Same	Same as No. 28-1			
29	gms moles m %	2028.80 20.0 17.3	18.24 0.12 0.10	0 0 0	11,160.50 50.0 43.5	11,083.50 45.2 39.1	24,301.04 115.32 99.8	Crystal Growth	10"	8"	1400	1300	1360	28
30	gms moles m %	2446.60 24.0 41.0	2.40 0.016 0.03	0 0 0	0 0 0	8240.0 33.6 58.9	10,689.20 57.62 99.9	Crystal Growth	10"	8"	---	1300	---	24
31	gms moles m %	1468.06 14.40 27.26	2.88 0.018 0.034	0 0 0	0 0 0	9416.06 38.4 72.70	10,887.02 52.82 99.99	Crystal Growth	10"	8"	---	1300	1340	24
32	gms moles m %	Same as No. 31, Not Run									---	---	---	---
33	gms moles m %	76.71 0.75 25.08	0.17 0.0011 0.017	7.59 0.040 1.34	0 0 0	540.00 2.20 73.58	624.47 2.99 100.4	Ga doped ruby	10" Hydra. Lab.	250 ml	1380	1300	1360	12
34	gms moles m %	81.60 0.80 33.33	0.1 0.001 0.046	0 0 0	0 0 0	352.32 1.60 66.66	474.06 2.40 100.3	Effect of higher con- centration of Al <sub>2</sub> O <sub>3</sub> on crystal growth	10" Hydro. Lab.	250 ml	---	1300	1365	24
35	gms moles m %	38.8	0.08	3.75	0	196.0	238.63	Not Run			---	---	---	---
36-1	gms moles m %	20.4 0.20 17.39	0.18 0.0012 0.10	0 0 0	111.6 0.50 43.3	110.8 0.43 39.1	242.98 1.15 99.8	Comparison of corro- sion of Pt. using PbO and Pb <sub>2</sub> O <sub>3</sub>	3"	100 ml	---	1300	---	24
36-2	gms moles m %	20.4 0.20 24.39	0.18 0.0012 0.15	0 0 0	116.6 0.17 20.73	110.8 0.54 54.88	247.98 0.82 100.2	Pb <sub>2</sub> O <sub>3</sub> wt. is reported in PbO column	3"	100 ml	---	1300	---	24
37	gms moles m %	4404.24 43.20 27.26	8.64 0.056 0.035	0 0 0	0 0 0	28,248.18 115.20 72.70	32,661.06 158.46 100.00	Effect of largest melt possible on crystal quality & Pt. corrosion	10"	8"	---	1300	1340	24
38	gms moles m %	40.8 0.40 33.33	0.08 0.0005 0.04	0 0 0	0 0 0	196.2 0.80 66.66	237.08 1.20 100.00	Effect of high Al <sub>2</sub> O <sub>3</sub> con- centration on crystal growth	10"	100 ml	---	1300	---	24
39	gms moles m %	4404.24 43.20 27.26	8.64 0.056 0.035	0 0 0	0 0 0	28,248.18 115.20 72.70	32,661.06 158.46 100.00	Large melt	10"	8"	---	1300	---	24

TABLE II

Run No.	Furnace Used	Crucible Used	Soak Temperature (°C)			Soak Time Hours	Cooling Rate °C/hr.	Pour Temperature		Crystal Yield		Flux Weight Loss %	Remarks
			Set	Pedestal	Plug			Pedestal	Plug	gm.	Percast		
No. 17, Percent	Lindberg	100 ml	1290	---	---	12	5	1) 800 2) 750 3) 760 4) 715 5) 700	---	---	---	---	Incomplete solution in every case.
Stirring during cycle.	10"	250 ml	1340	1280	---	4	5	700	---	---	---	---	Incomplete solution.
Rep make growth	10"	12"	---	---	---	---	---	---	---	---	---	---	Crucible failed.
Quality of 100% PbF <sub>2</sub>	10"	100 ml	---	1300	20	20	9	1000	---	9.75	31	15	Good quality flux free crystal. Very heavy Cr concentration.
25-1	Same	Same	Same as No. 25-1							---	---	8.9	Incomplete solution.
25-1	Same	Same	Same as No. 25-1							---	---	33	Incomplete solution.
25-1	Same	Same	Same as No. 25-1							---	---	39	Incomplete solution.
Quality of 100% PbF <sub>2</sub>	10"	250 ml	1330	1300	---	24	4	925	---	---	---	---	Stirring during growth caused small, badly formed crystals.
26-1	Same	Same	Same as No. 26-1										
26-1	10"	100 ml	Same as No. 26-1										
Al <sub>2</sub> O <sub>3</sub> from	10"	5 1/4"	---	1220	---	---	---	1060	---	---	---	13	Incomplete solution.
100% PbF <sub>2</sub>	10"	250 ml	1380	1305	1360	24	5	940	---	---	---	25	Flux solidified before pour because of pedestal sticking in furnace. Stirring again caused poor crystal quality.
28-1	Same	Same	Same as No. 28-1									21	
28-1	Same	Same	Same as No. 28-1									30	
With	10"	8"	1400	1300	1360	28	5	---	---	---	---	---	Incomplete solution.
With	10"	8"	---	1300	---	24	5	---	---	---	---	---	Incomplete solution.
With	10"	8"	---	1300	1340	24	1.5	1060	1100	385.24	26.2	---	Good crystal growth, no premelting used.
by	10" Hydro. Lab.	250 ml	1380	1300	1360	12	5	1000	---	38.5	33.3	20	Good crystal growth and small additional phases.
Char con- of Al <sub>2</sub> O <sub>3</sub> on with	10" Hydro. Lab.	250 ml	---	1300	1365	24	5	---	---	---	---	---	Cover came off crucible and PbF <sub>2</sub> evaporated.
and corrosion using PbO	3"	100 ml	---	1300	---	24	5	1065	---	---	---	---	Crucible spilled.
Reported one	3"	100 ml	---	1100	---	24	5	1065	---	---	---	30	Crystal growth. No visible corrosion in 100 ml crucible.
Largest melt crystal corrosion	10"	8"	---	1300	1340	24	1.5	---	---	---	---	---	Crucible failed and possible spillage from overfilling.
Al <sub>2</sub> O <sub>3</sub> con- on crystal	10"	100 ml	---	1300	---	24	5	---	---	---	---	---	Incomplete solution.
	10"	8"	---	1300	---	24	1.5	---	---	---	---	---	Can overflowed.

B

TABLE II (CONTINUED)

40	Same Weight as No. 39						Same as No. 39				Same as No. 39						
41	Same Weight as No. 39						Same as No. 38				1400	1300	---	12	5		
42-1	gms	30.6	0.0	0	0	196.2	226.8	Solubility of Al <sub>2</sub> O <sub>3</sub> in PbF <sub>4</sub>	Lindberg	100 ml	---	1100	---	24	0		
	moles	0.30	0.0	0	0	0.80	1.16										
	m %	27.27	0.0	0	0	72.73	100.00										
42-2	Same Weight as No. 42-1						Same as No. 42-1				--	1100 1200	---	48 24	0		
42-3	Same Weight as No. 42-2						Same as No. 42-2				---	1100 1200	---	48 24	0		
43	gms	3293.08	3.24	0	0	21,146.48	24,442.80	1/4 reduction in wt. of No. 39, Cr conc. reduced by one-half	10"	8"	---	1300	---	12	1.5		
	moles	32.30	0.021	0	0	86.24	118.56										
	m %	27.24	0.0177	0	0	72.74	100.00										
44	gms	40.8	0.0	0	0	196.2	237.0	Solubility of Al <sub>2</sub> O <sub>3</sub> in PbF <sub>4</sub>	Lindberg	100 ml	---	---	---	---	---		
1-3	moles	0.40	0.0	0	0	0.80	1.20										
	m %	33.33	0.0	0	0	66.66	99.99										
45-1	gms	40.8	0.0	0	0	196.2	237.0	Solubility of Al <sub>2</sub> O <sub>3</sub> in PbF <sub>4</sub>	Lindberg	100 ml	---	1280	---	24	0		
	moles	0.40	0.0	0	0	0.80	1.20										
	m %	33.33	0.0	0	0	66.66	99.99										
45-2	Same Weight as No. 45-1						Same as No. 45-1				---	---	---	---	---		
45-3	Same Weight as No. 45-1						Same as No. 45-1				---	1280 1400	---	36 24	0		
46	gms	3293.08	3.24	0	0	21,146.48	24,442.80	Effect of 4.5 gms Al <sub>2</sub> O <sub>3</sub> seed on crystal growth	10"	8"	1400	1300	1330	12	2		
	moles	32.30	0.021	0	0	86.24	118.56										
	m %	27.24	0.0177	0	0	72.74	100.00										
47	gms	81.6	0.16	0	0	392.4	474.16	Solubility of Al <sub>2</sub> O <sub>3</sub> in PbF <sub>4</sub>	3"	250 ml	---	1350	---	16	25		
	moles	0.80	0.0011	0	0	1.60	2.40										
	m %	33.33	0.046	0	0	66.66	100.0										
48	Same Weight as No. 47						Same				Same	Same	---	1400	---	16	25
49	gms	88.0	0.08	0	0	392.4	480.56	Seeded crystal growth wt. of Al <sub>2</sub> O <sub>3</sub> includes seed of 6.40 gms.	3"	250 ml	---	1400	---	8	25		
	moles	0.86	0.0005	0	0	1.60	2.46										
	m %	34.96	0.020	0	0	65.04	100.0										
50	gms	3293.11	3.24	0	0	21,146.69	24,443.34	Effect of temperature gradient on crystal growth	10"	8"	---	1300	---	---	---		
	moles	32.30	0.021	0	0	86.24	118.56										
	m %	27.24	0.0177	0	0	72.74	100.00										
51	gms	90.0	0.0	0	0	392.4	482.4	Solubility of Al <sub>2</sub> O <sub>3</sub> in PbF <sub>4</sub>	3"	250 ml	---	1400	---	7	25		
	moles	0.88	0.0	0	0	1.60	2.48										
	m %	35.48	0.0	0	0	65.25	100.73										
52	gms	90.0	0.0	0	0	392.4	482.4	Solubility of Al <sub>2</sub> O <sub>3</sub> in PbF <sub>4</sub>	3"	250 ml	---	1400	---	3	0		
	moles	0.88	0.0	0	0	1.60	2.48										
	m %	35.48	0.0	0	0	65.25	100.73										
53	gms	100.0	0.0	0	0	392.4	492.4	Solubility of Al <sub>2</sub> O <sub>3</sub> in PbF <sub>4</sub>	3"	250 ml	---	1400	---	16	---		
	moles	0.97	0.0	0	0	1.60	2.57										
	m %	37.74	0.0	0	0	62.26	100.0										
54	gms	40.8	0.04	0	0	196.2	237.04	Effect of Cr on sol. of Al <sub>2</sub> O <sub>3</sub> in PbF <sub>4</sub>	Lindberg	100 ml	---	1200 1300 1400	---	24	---		
1-3	moles	0.40	0.0003	0	0	0.80	1.20										
	m %	33.33	0.03	0	0	66.66	100.02										
55	Not Run											---	---	---	---	---	
1-6																	
56	gms	3293.11	3.24	0	0	21,146.69	24,443.04	Crystal Growth	10"	8"	1350	1300	---	12	2.0		
	moles	32.30	0.021	0	0	86.24	118.56										
	m %	27.24	0.0177	0	0	72.74	100.00										
57	gms	81.6	0.0	0	0	392.4	474.16	Solubility of Al <sub>2</sub> O <sub>3</sub> in PbF <sub>4</sub>	3"	250 ml	1500	1400	---	16	0		
	moles	0.80	0.0	0	0	1.60	2.40										
	m %	33.33	0.0	0	0	66.66	99.99										
58	gms	80.0	0.0	0	0	313.9	393.9	Solubility of Al <sub>2</sub> O <sub>3</sub> in PbF <sub>4</sub>	3"	250 ml	1500	1400	---	15	0		
	moles	0.78	0.0	0	0	1.28	2.06										
	m %	37.86	0.0	0	0	62.13	99.99										
59	Not Run											---	---	---	---	---	

TABLE II (CONTINUED)

[illegible]





TABLE II

Purpose of Run	Furnace Used	Crucible Used	Soak Temperature (°C)			Gradient during cooling (°C)	Soak Time (hours)	Cooling Rate (°C/hr)	Pour Temperature (°C)		Crystal Yield		Flux Weight (grams)
			Pedestal	Plug	Set				Pedestal	Plug	Grams	Percent	
Crystal growth	10"	8"	1395	----	1450	-20	12	0.5	1200°C	---	----	----	----
Solubility data	(1) Lindberg	100 ml	----	----	1300	--	96	0	----	----	----	----	4.55
	(2) Lindberg	100 ml	----	----	1205	--	72	0	----	----	----	----	5.45
	(3) Lindberg	100 ml	----	----	1000	--	24	0	----	----	----	----	6.50
	(4) Lindberg	100 ml	----	----	1105	--	48	0	----	----	----	----	29.00
	(5) Lindberg	100 ml	----	----	1395	--	120	0	----	----	----	----	47.20
Solubility data	No. 5 H. T. L.	250 ml	----	----	1400	--	16	0	1400°C	----	----	----	40.00
Effect of ruby seeds (total wt. = 42 gms) on nucleation	10"	8"	1400	----	1450	--	12	5	1100°C	----	----	----	----
Effect of ruby seeds (71.3) on crystal growth	10"	8"	1400	----	----	--	--	--	----	----	----	----	----
Test effectiveness of analytical procedures	5"	250 ml	1400	----	1500	--	16	0	1400°C	----	----	----	13.7
Solubility data	5"	250 ml	1320	----	----	--	16	0	1320°C	----	----	----	93.0
Solubility data	5"	250 ml	1320	----	----	--	16	0	1320°C	----	----	----	8.3
Solubility data	5"	250 ml	1000	----	----	--	15	0	1000°C	----	----	----	8.7
Solubility data	5"	250 ml	1000	----	----	--	16	0	1000°C	----	----	----	12.4
Solubility data	5"	250 ml #104	1400	----	----	--	12	0	1090°C	----	32.6	44.4	4.2
	5"	250 ml #102	1400	----	----	--	12	0	1190°C	----	----	----	----
	5"	250 ml #115	1400	----	----	--	12	0	925°C	945	45.8	62.4	27.1
	5"	250 ml #117	1400	----	----	--	12	0	1350°C	----	10.0	13.6	----
	5"	250 ml #105	1400	----	----	--	12	0	1240°C	1290	17.9	24.4	51.7
	5"	250 ml #118	1400	----	----	--	12	0	1000°C	1040	----	----	----
Solubility data	Lindberg	100 ml	----	----	900	--	16	12	800°C	----	----	----	----
Effect of ruby seeds (13.9 gms) on crystal growth	10"	8"	1400	1300	1460	-100	12	1.0	1000°C	----	800	58.9	2358
Effect of ruby seeds (71.3 gms) on crystal growth	10"	8"	1400	1430	1460	30-210	12	1.5	940°C	1150	2273	55.7	1145
Solubility data	Lindberg	100 ml	----	----	----	--	--	--	----	----	----	----	----
Solubility data	5"	250 ml #121	1400	----	----	--	18	2.5	1350°C	----	0.32	0.44	23.1
		250 ml #122	----	----	----	--	12	2.5	1240°C	----	24.0	32.7	56.7
		250 ml #123	----	----	----	--	--	--	----	----	----	----	----
		250 ml #124	----	----	----	--	12	--	1311°C	----	15.3	20.8	27.0
		250 ml #125	----	----	----	--	12	--	1190°C	----	25.9	35.3	51.2
		250 ml #126	----	----	----	--	6	--	1150°C	----	----	----	----
		250 ml #127	----	----	----	--	6	--	1000°C	----	48.3	65.8	191.5
		250 ml #128	----	----	----	--	12	--	1150°C	----	28.7	39.1	22.6
		250 ml #129	----	----	----	--	6	--	1100°C	----	33.0	45.0	45.4
		250 ml #130	----	----	----	--	--	--	----	----	----	----	----
Effect of ruby seed (79.4 gms) on crystal growth	10"	8"	1400	1430	1460	370	8 1/2	1.5	970°C	1340	1590.9	39.0	----
Same as Run No. 64	10"	8"	1400	1430	1460	--	7 1/2	--	----	----	----	----	----
Same as Run No. 64	10"	8"	----	----	----	--	--	--	----	----	----	----	----
Same as Run No. 64	10"	8"	1400	1430	1460	200	7 1/2	1.5	1000°C	----	1243	30	----
Effect of premelting on 250 ml crucible	5"	250 ml	1400	----	----	--	12	--	1000°C	----	----	----	----
Effect of premelting on 250 ml crucible	5"	250 ml	1400	----	----	--	12	--	1000°C	----	----	----	----

Run (C)	Soak Time (hours)	Cooling Rate (°C/hr)	Pour Temperature (°C)		Crystal Yield		Flux Weight Loss		Remarks
			Pedestal	Plug	Grams	Percent	Grams	Percent	
	12	0.5	1200°C	---	---	---	---	---	Good crystals, thin plates with very few flux inclusions, heavy Cr dopant concentration, cover came off 8" can during run.
	96	0	---	---	---	---	4.55	2.3	
	72	0	---	---	---	---	5.45	2.7	
	24	0	---	---	---	---	6.50	3.3	
	48	0	---	---	---	---	29.00	14.8	
	120	0	---	---	---	---	47.20	24.1	
	16	0	1400°C	---	---	---	40.00	12.7	Slight spillage.
	12	5	1100°C	---	---	---	---	---	Pt can developed leaks.
	--	--	---	---	---	---	---	---	Alumina plug broke and fell on crucible.
	16	0	1400°C	---	---	---	13.7	3.5	-----
	16	0	1320°C	---	---	---	93.0	22.7	-----
	16	0	1320°C	---	---	---	8.3	2.1	-----
	16	0	1000°C	---	---	---	8.7	2.2	-----
	16	0	1000°C	---	---	---	12.4	3.2	-----
	12	0	1090°C	---	32.6	64.4	4.3	1.2	Slightly underdiscoided.
	12	0	1190°C	---	---	---	---	---	Slight spillage.
	12	0	925°C	945	45.8	62.4	27.1	7.7	-----
	12	0	1350°C	---	10.0	13.6	---	---	Incomplete solution.
	12	0	1240°C	1290	17.9	24.4	51.7	14.6	-----
	12	0	1000°C	1040	---	---	---	---	-----
	15	12	800°C	---	---	---	---	---	Incomplete solution, remainder of run failed.
	12	1.0	1000°C	---	800	58.9	2358	36	Thin ruby plates, seed dissolved.
	12	1.5	940°C	1150	2273	55.7	1145	5	Thick ruby plates, seed dissolved.
	--	--	---	---	---	---	---	---	Run failed when Pt. crucibles reacted with SiC muffle.
	18	2.5	1350°C	---	0.32	0.44	23.1	5.4	-----
	12	2.5	1240°C	---	24.0	32.7	56.7	13.3	Pt. cover opened slightly.
	--	--	---	---	---	---	---	---	Plug broke and fell on crucible.
	12	--	1311°C	---	15.3	20.8	27.0	6.3	-----
	12	--	1190°C	---	25.9	35.3	51.2	12.0	-----
	6	--	1150°C	---	---	---	---	---	Incomplete solution.
	6	--	1000°C	---	48.3	65.8	191.5	44.9	Cover opened.
	12	--	1150°C	---	28.7	39.1	22.6	5.3	-----
	6	--	1100°C	---	33.0	45.0	45.4	10.6	-----
	--	--	-----	-----	-----	-----	-----	-----	-----
	8 1/2	1.5	970°C	1340	1590.9	39.0	---	---	Seed came loose and floated to top of melt, no growth on seed.
	7 1/2	--	---	---	---	---	---	---	Pt. can failed.
	--	--	---	---	---	---	---	---	Programmer not set, run poured after 20 hr. soak.
	7 1/2	1.5	1000°C	---	1223	30	---	---	Growth on seed achieved as series of plates. Pt can failed.
	12	--	1000°C	---	---	---	---	---	Furnace failure.
	12	--	1000°C	---	---	---	---	---	Furnace failure.

C

Run No.	Composition					Totals	Purpose
	Mol. Wts. Units	101.96 $\text{Al}_2\text{O}_3$	152.02 $\text{Cr}_2\text{O}_3$	187.44 $\text{Ga}_2\text{O}_3$	245.21 $\text{PbF}_2$		
79.	gms	3,675.0	0.30	0.00	20,000.0	23075.30	Effect of seed (43.3 gms) on growth
	moles	30.17	0.002	0.00	81.56	111.73	
	m%	27.00	0.002	0.00	73.00	100.00	
80.	gms	4,077.60	0.40	0.00	19,618.80	23696.40	Growth on ruby seed (221.3 gms)
	moles	40.00	0.0026	0.00	81.54	121.54	
	m%	32.91	0.002	0.00	57.10	100.00	
81.	gms	5,709.09	0.56	0.00	13,731.80	19,440.39	Growth on ruby seed (221.3 gms)
	moles	56.00	0.0037	0.00	56.00	112.00	
	m%	50.00	0.003	0.00	50.00	100.00	
82.	gms	4,545.40	0.00	0.00	19,545.40	24090.80	Growth on a ruby seed using ruby nutrient
	moles	44.59	0.00	0.00	79.71	124.30	
	m%	35.87	0.00	0.00	64.13	100.00	
83. 1-9	See Table II for details						Solubility of $\text{Al}_2\text{O}_3$ in
84. 1-12	See Table II for details						Solubility of $\text{Al}_2\text{O}_3$ in
85.	gms	4,545.40	0.00	0.00	19,545.40	24090.80	Growth on ruby seed (221.3 gms) using ruby nutrient
	moles	44.59	0.00	0.00	79.71	124.30	
	m%	35.87	0.00	0.00	64.13	100.00	
86.	gms	4,545.40	0.00	0.00	19,545.40	24090.80	Growth on ruby seed (221.3 gms) using ruby nutrient
	moles	44.59	0.00	0.00	79.71	124.30	
	m%	35.87	0.00	0.00	64.13	100.00	
87.	gms	73.4	0.007	0.00	346.0	433.4	Effect of 14 gms $\text{B}_2\text{O}_3$ on $\text{PbF}_2$ flux and on $\text{Al}_2\text{O}_3$ growth
	moles	0.72	0.00004	0.00	1.41	2.13	
	m%	33.80	0.002	0.00	66.24	100.042	

TABLE II

Purpose	Furnace	Crucible	Soak		Temp(°C)		Gradient during cooling (°C)	Soak Time (hrs)	Cooling Rate (°C/hr)	Pour Temp °C	
			Ped.	Plug	Set					Ped	Plug
seed (17.3 gns)	10"	8"	1160	1260	1300	100°C	60	0		1160	1260
ruby seed (29	10"	8"	1220	1300	1300	80	60	0		1220	1300
ruby seed (248.6	10"	8"	--	--	--	--	--	--		--	--
a ruby seed nutrient	10"	8"	--	--	1300	--	--	--		--	--
of Al <sub>2</sub> O <sub>3</sub> in PbF <sub>2</sub>	3"	250 ml	1400	--	--	--	--	--		--	--
of Al <sub>2</sub> O <sub>3</sub> in PbF <sub>2</sub>	3"	250 ml	1400	--	--	--	--	--		--	--
ruby seed (e) using ruby	10"	8"	1230	1140	1250	90	72	10		1030	940
ruby seed (183 ruby nutrient	10"	8"	1265	1205	1300	65	672	0		1265	1205
4 gms B <sub>2</sub> O <sub>3</sub> flux and on th	3"	250 ml	1400	--	--	--	2	4		1000	--

<u>Pour Temp °C</u>		<u>Crystal Yield</u>		<u>Flux Wt. loss</u>		<u>Remarks</u>
<u>Ped</u>	<u>Plug</u>	<u>Gms</u>	<u>%</u>	<u>Gms</u>	<u>%</u>	
1160	1260	0	0	--	--	Seed dissolved and no crystals grew. O <sub>2</sub> used and no visible corrosion in pt can after run. Rotation on during entire run.
1220	1300	0	0	--	--	Seed dissolved. Small excess Al <sub>2</sub> O <sub>3</sub> powder on base of crucible. Very little corrosion observed in pt crucible. O <sub>2</sub> used.
--	--	--	--	--	--	R n failed due to leaky can. Can had failed previously and had had a new base added. The joint failed and the can was scraped.
--	--	--	--	--	--	Wt sh n for Al <sub>2</sub> O <sub>3</sub> is actually ruby. This ruby was from previous crystal growth runs. No significant growth deposited on seed, but neither it nor nutrient dissolved completely.
--	--	--	--	--	--	Table III contains details of these experiments.
--	--	--	--	--	--	Table III contains details of these experiments.
1030	940	0	0	--	--	Very little growth. No large crystals.
1265	1205	--	--	--	--	Much growth but not single crystal. No apparent Cr concentration gradient. Much platey growth on seed & undissolved crust.
1000	--	38.5	--	--	--	Very large flux free ruby plates.

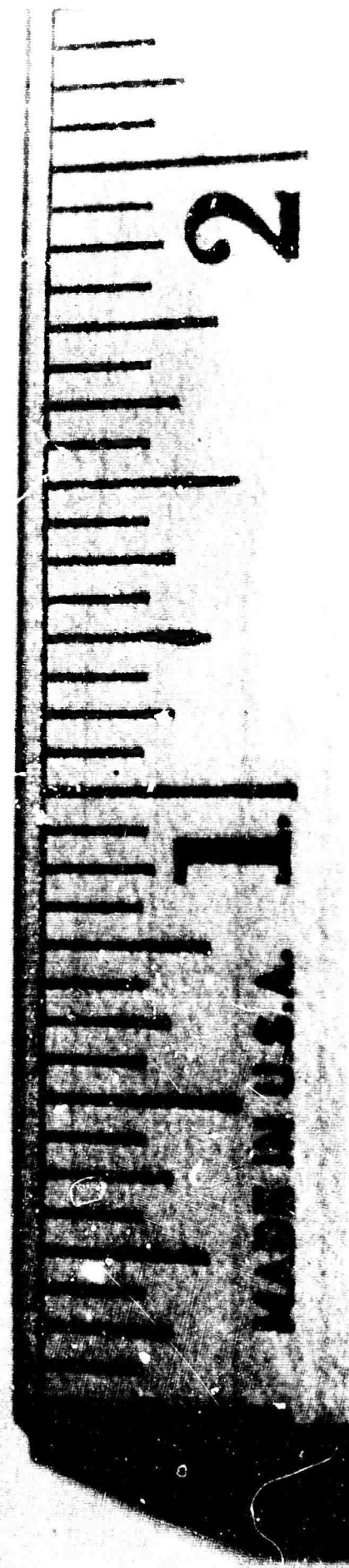


Figure 1 - Flux Included Flate of Ruby

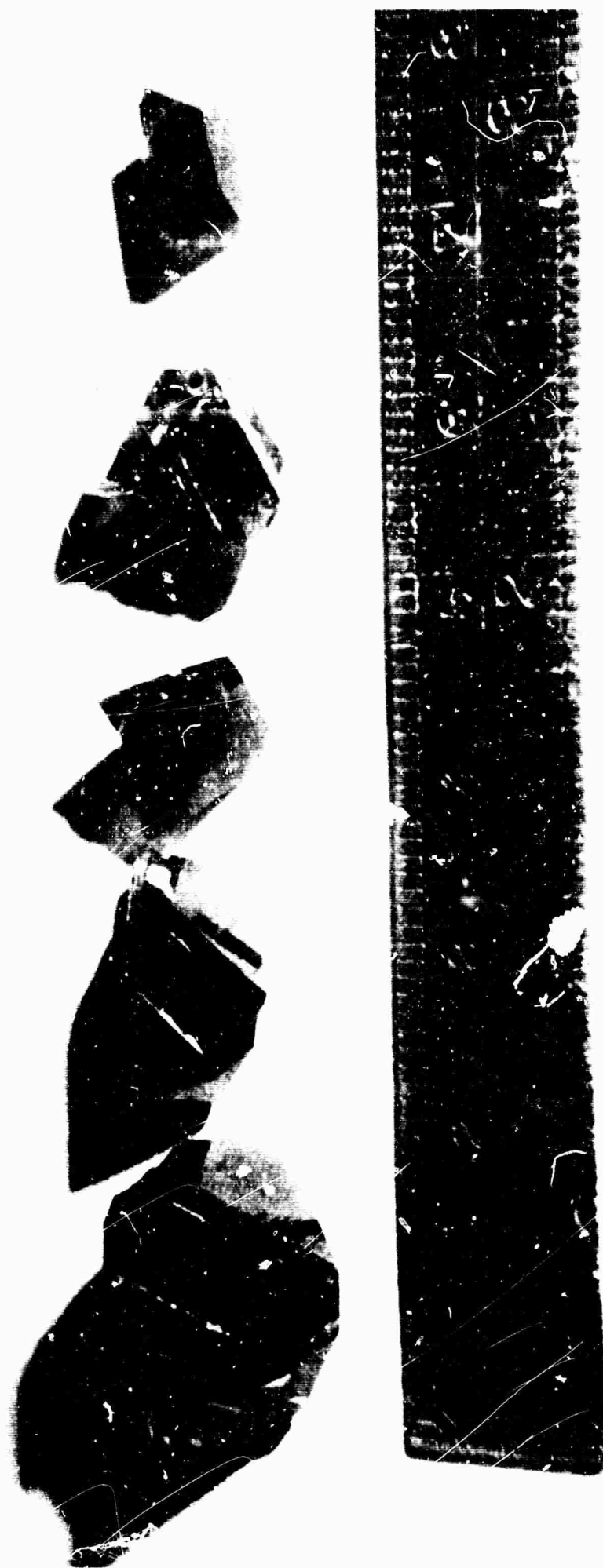


Figure 2 - Ruby Crystals Rhombohedral



Experimental (Cont.)

plates. These thick plates were usually found at, or near, the bottom of the crucible. As suggested by Linares<sup>(2)</sup>, replacing  $\text{PbF}_2$  with  $\text{PbO}$  favored the crystallization of thick plates, but only at the expense of sharply reduced  $\text{Al}_2\text{O}_3$  solubility. The problem, therefore, was to define growth conditions which control plate thickness.

A number of runs were made in which the vertical gradient was varied both in direction and magnitude. Runs No. 50, 60 63, 64, 7C, and 71 were designed to determine the effect, if any, of temperature gradient on plate thickness. Early runs were generally made with the supporting pedestal about  $30^\circ\text{C}$  cooler than the plug, and the crucible was positioned so that the top was as close as possible to the bottom of the upper furnace plug. It was felt that the temperature difference as measured at the pedestal and plug would at least bear some relation to the internal gradient in the melt. In Runs No. 50, 60, 63, and 64, where there were small temperature differences in either direction, or where the pedestal was hotter than the plug, very thin plates were grown. It was felt that a large gradient was desirable, but this was difficult to obtain because of the high temperature involved. If a temperature difference of  $200^\circ\text{C}$  was needed, for example, with a pedestal temperature of  $1400^\circ\text{C}$ , a plug temperature of  $1600^\circ\text{C}$  would be required. This temperature is, of course, beyond the design limitations of the furnace. This problem was solved by imposing the gradient only after the soak period was completed. This was accomplished by slowly lowering the

Experimental (Cont.)

pedestal until the proper temperature difference was achieved. At this point, the cooling cycle was begun.

The growth procedure used was as follows: 33.33 m percent  $\text{Al}_2\text{O}_3$  in  $\text{PbF}_2$  were heated with stirring to  $1400^\circ\text{C}$  in a Pt crucible for a sufficient time to insure complete solution usually in about 4 hours. Stirring was accomplished during the soak period by rotating the pedestal first in one direction and then in the other. This procedure aided in the rapid solution of the  $\text{Al}_2\text{O}_3$ . Oxygen was pumped into the furnace during the entire run. The pedestal was then slowly lowered to a position sufficient to produce a  $200^\circ\text{C}$  temperature difference from top to bottom of the crucible, with the top maintained at  $1400^\circ\text{C}$ . The bottom of the crucible was cooled at no more than  $1.5^\circ\text{C}$  per hour to  $1200^\circ\text{C}$  at which point the entire furnace was cooled at  $1.5^\circ\text{C}$  per hour to  $1000^\circ\text{C}$ . The molten lead fluoride was decanted at  $1000^\circ\text{C}$  and the crystals were washed in 50 percent  $\text{HNO}_3$ .

It appeared that when ruby was crystallized from  $\text{PbF}_2$  a condition of high supersaturation existed prior to nucleation. When nucleation did occur, many small crystals formed, which grew rapidly as thin plates, trapping flux between adjacent layers. Much of this growth was very loosely attached to the crucible, if at all, and was free to float to the surface of the melt. If the surface of the melt was cooler than the bottom, these poor quality crystals grew faster than those adhering to the base or walls of the crucible below the surface of the melt. But if the top were maintained

Experimental (Cont.)

considerably hotter than the bottom, this initial nucleation in the form of very thin plates redissolved at the top of the melt, leaving only the higher quality slower growing ruby which was firmly attached to the base and walls of the Pt crucible. Further improvement in the size and quality of ruby crystals was achieved by the addition of 3 percent  $B_2O_3$  to  $PbF_2$ .  $B_2O_3$  seems to have the same favorable effect on ruby that Van Uitert<sup>(3)</sup> has reported for yttrium aluminum garnet. The  $B_2O_3$  apparently reduces the ability of the flux to supersaturate.

While improvement in crystal size and quality was observed using spontaneous nucleation techniques described above, it was felt that still better results and better control could be achieved through the use of ruby seeds. Therefore, attempts to grow ruby on a seed were begun.

2. Growth on Seeds

Attempts to produce significant growth on a ruby seed were made in Runs No. 63, 64, 70, 71, 74, 75, 76, and 77 by slowly cooling a melt from 1400°C to 1000°C. Because of the large difference in weight between the  $Al_2O_3$  powder added as nutrient and the ruby crystals available as seeds, it was necessary to define soak conditions much more precisely than previously to avoid dissolution of the seed. It was also necessary to keep the seed on the bottom of the melt since ruby floats in molten  $PbF_2$ ; the seed was tied to a platinum sheet with platinum wire. In all the early attempts, the seeds dissolved. Run No. 77 was the first partially successful attempt. Here a

Experimental (Cont.)

platinum wire was passed through a hole drilled in a flame fusion ruby of 32 grams. Similar weights and conditions were employed as in No. 74. We succeeded in obtaining about 20 grams of growth on the seed. A large part of this growth was in the form of epitaxially attached parallel plates, instead of the solid single crystal growth we had hoped for.

Several additional attempts to obtain growth using a seed tied to the bottom of the crucible and the bottom maintained cooler than the top were not successful. In each case, the seed dissolved or growth was dendritic.

Finally in Runs No. 82 and 85, a positive gradient with the plug cooler than the pedestal was used. A Pt baffle, which served to hold solid pieces of ruby nutrient on the bottom of the can was used, with a large ruby seed attached above the baffle. The melt was soaked at 1250°C for 3 days with rotation, then cooled to 1000°C at 1°C per hour. Very little growth was present on the seed, and what was present was not one single crystal.

One final run (No 86) was made using a positive gradient and ruby nutrient held behind a protective baffle. This time no cool down was made so that growth would be entirely due to circulation of solvent. A 4 week soak with rotation at 1270°C was followed by a pour at 1270°C. A crust had formed on the surface, which had served as nucleation centers for many small crystals of high quality. The seed crystal was covered with the usual array of small plates.

Experimental (Cont.)

It would appear that successful growth of ruby crystals on seeds will require very accurate control of gradients within the crucible as well as circulation of the melt and cooling rates. White<sup>(1)</sup> reports that while small scale growth up to 5 mm on seed crystals has been achieved, larger scale growth up to 25 mm has been of poor quality. He feels that seed quality and growth rate are important parameters.

B. Solubility Studies

Runs No. 73, 83, and 84 were made to determine the solubility of  $\text{Al}_2\text{O}_3$  in  $\text{PbF}_2$  and the effect of Cr on this solubility. Some experimentation was necessary before a successful method was produced. The main difficulties associated with solubility determination in flux systems are to ensure that equilibrium conditions are reached and to eliminate evaporation as a factor. The term "solubility" should be put in quotes when referring to ruby since we are precipitating a dilute solid solution of  $\text{Cr}_2\text{O}_3$  in  $\text{Al}_2\text{O}_3$  and there is a distribution of  $\text{Cr}_2\text{O}_3$  between the solid and liquid phases which is proportional to the amount of chromium oxide dissolved in the liquid solution.

1.  $\text{PbF}_2$ - $\text{Al}_2\text{O}_3$  System

Giess<sup>(4)</sup> and White<sup>(1)</sup> measured the solubility of  $\text{Al}_2\text{O}_3$  in  $\text{PbF}_2$  by measuring the loss in weight of a sapphire rod immersed in  $\text{PbF}_2$  enclosed in a sealed platinum tube. The major problems were with vapor leaks which were detected by weighing before and after heating, and insure

Experimental (Cont.)

that equilibrium conditions actually existed. White reported that equilibrium was attained after about 16 hours at 1200°C, but the problem of vapor leaks prevented temperatures in excess of 1250 degrees from being measured using this technique.

Because of the difficulties experienced in completely sealing the Pt tubes, a second technique similar to the one developed at Airtron was used by White. This technique consisted of heating pieces of corundum in a crucible for appropriate times at each temperature, then quenching and analyzing pieces of the resulting solid for alumina content.

White reported 25.6 mole percent  $\text{Al}_2\text{O}_3$  solubility at 1200°C, and Giess' value was 26.6. A curve of Giess' and White's values are shown in Figure 3. It can be seen that both these curves are apparently straight lines. However, neither White nor Giess were able to measure the solubility of  $\text{Al}_2\text{O}_3$  in  $\text{PbF}_2$  at temperatures above 1300°C. Two runs were made by us, one at 1350°C and one at 1300°C to determine the solubility of  $\text{Al}_2\text{O}_3$  in this region. These values are consistent with an extrapolation of Giess' curve.

2.  $\text{PbF}_2$  - Dilute Ruby

Solubility of dilute ruby in  $\text{PbF}_2$  was measured in a number of runs summarized in Table III. Best results were obtained when  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  were dissolved in  $\text{PbF}_2$  at 1400°C with rotation. The furnace was slowly cooled to a specified temperature, and the melt, which was decanted into a platinum crucible immersed in cold water, was analyzed for  $\text{Al}_2\text{O}_3$ . This

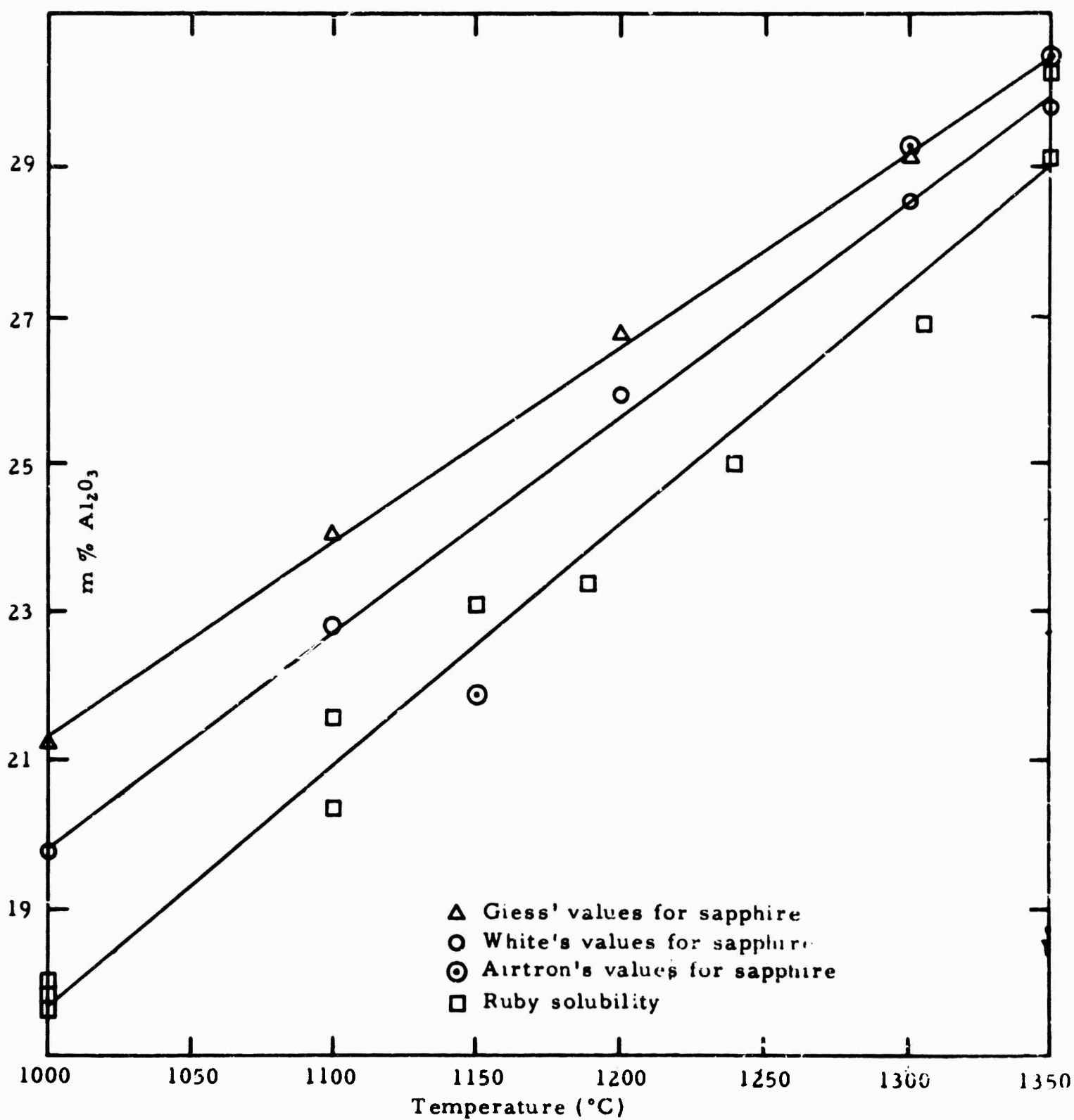


Figure 3  
Comparison of Ruby and Sapphire Solubility in PbF<sub>2</sub>

TABLE III

Run #	mol wts Units	Composition				Run #	Soak Time (hrs.)	Temp. (°C)		207.71 %Pb	245.21 PbF <sub>2</sub> (calc)	Flux		Analysis		Total	%Pb	Cry. Al <sub>2</sub> O <sub>3</sub> (by diff)
		101.96 Al <sub>2</sub> O <sub>3</sub>	152.02 Cr <sub>2</sub> O <sub>3</sub>	187.44 Ga <sub>2</sub> O <sub>3</sub>	245.21 PbF <sub>2</sub>			Soak	Quench			245.21 PbF <sub>2</sub> (by diff)	101.96 Al <sub>2</sub> O <sub>3</sub>	152.02 Cr <sub>2</sub> O <sub>3</sub>	137.44 Ga <sub>2</sub> O <sub>3</sub>			
73	gms	73.4	0.07	0.00	353.2	426.47	73-1	18	1400 1350	70.21	83.05	85.02	14.96	0.003	6.00	100.00	18.17	99.816
1-9	moles	0.72	0.0004	0.00	1.44	2.16						0.347	0.15	0.00002	0.00	0.497		0.979
	m%	33.33	5.02	0.00	66.66	100.01						69.82	10.18	0.004	0.00	100.00		99.89
							73-2	12	1400 1240	73.72	87.23	88.18	11.80	0.003	0.00	100.00	4.58	99.893
												0.360	0.12	0.00002	0.00	0.480		0.980
												75.00	25.00	0.004	0.00	100.00		99.92
							73-3											
							73-4	12	1400 311	71.96	87.52	85.25	13.75	0.00	0.00	100.00	3.50	99.803
												0.352	0.14	0.00	0.00	0.482		0.979
												73.63	26.37	0.004	0.00	100.00		99.86
							73-5	12	1400 1190	73.12	88.79	88.36	11.64	0.00	0.00	100.00	2.05	99.865
												0.360	0.11	0.00	0.00	0.470		0.980
												75.60	23.40	0.00	0.00	100.00		99.90
							73-6	6	1400 1150	74.61	88.24		12.42					
							73-7	6	1400 1000	78.95	93.42	92.05	7.94	0.00	0.00	100.00	1.90	99.890
												0.375	0.08	0.00	0.00	0.455		0.980
												82.42	17.58	0.00	0.00	100.00		99.92
							73-8	12	1400 1150	75.87	89.78	89.33	10.47	0.00	0.00	100.00	3.42	99.913
												0.364	0.11	0.00	0.00	0.474		0.980
												76.79	23.21	0.00	0.00	100.00		99.83
							73-9	6	1400 1100	75.52	89.36	89.52	10.47	0.00	0.00	100.00	2.37	99.905
												0.365	0.10	0.00	0.00	0.465		0.980
												78.49	21.51	0.00	0.00	100.00		99.83
83	Same wts as 73 above					83-1												
1-9						83-2												
						83-3	1	1400 1000		82.41	97.52	91.57	8.40	0.016	0.00	100.00	6.76	99.942
												0.373	0.082	0.00030	0.00	0.455		0.980
												81.98	18.02	0.002	0.00	100.00		99.95
						83-4	1	1400 1350		73.60	87.10	85.42	14.56	0.004	0.00	100.00	2.71	99.770
												0.348	0.143	0.00003	0.00	0.491		0.979
												70.88	29.12	0.006	0.00	100.00		99.84
						83-5	1	1400 1150		77.80	92.07	89.57	10.43	0.00	0.00	100.00	5.29	100.00
												0.365	0.102	0.00	0.00	0.467		0.981
												78.16	21.84	0.00	0.00	100.00		100.00
						83-6	1	1400 1150		80.76	95.81	89.82	10.16	0.00	0.00	100.00	1.13	100.00
												0.366	0.100	0.00	0.00	0.466		0.981
												78.54	21.46	0.00	0.00	100.00		100.00
						83-7												
						83-8	1	1400 1100		78.76	93.20	90.40	9.60	0.00	0.00	100.00	1.75	99.892
												0.369	0.094	0.00	0.00	0.463		0.900
												79.70	20.30	0.00	0.00	100.00		99.82
						83-9	1	1400 1000		75.23	89.03	91.70	8.28	0.00	0.00	100.00	1.34	99.890
												0.374	0.081	0.00	0.00	0.455		0.980
												82.20	17.80	0.00	0.00	100.00		99.82
84	gms	73.4	0.00	1.87	353.2	428.47	84-1	1	1400 1270	74.08	87.67	84.82	14.69	0.00	0.49	100.00	4.71	98.38
1-12	moles	0.72	0.00	0.01	1.44	2.17	A					0.346	0.144	0.00	0.003	0.497		0.965
	m%	33.18	0.00	0.46	66.36	100.00						70.18	29.21	0.00	0.61	100.00		99.07
	gms	73.4	0.00	7.87	353.2	434.47	84-2	1	1400 980	78.11	92.43	80.37	9.12	0.00	0.40	100.00	10.99	95.006
	moles	0.72	0.00	0.04	1.44	2.20	B					0.328	0.089	0.00	0.002	0.419		0.932
	m%	32.73	0.00	1.82	65.45	100.00						78.28	21.24	0.00	0.48	100.00		97.18
	gms	73.4	0.07	1.87	353.2	428.54	84-3	1	1400 1000	77.76	92.02	90.43	9.33	0.00	0.24	100.00	3.22	98.41
	moles	0.72	0.0004	0.01	1.44	2.17	C					0.349	0.092	0.00	0.001	0.462		0.965
	m%	33.18	0.02	0.46	66.66	100.32						70.18	19.91	0.00	0.22	100.00		99.07
	gms	73.4	0.00	0.00	353.2	426.6	84-4	1	1400 1200	73.95	87.51	86.24	12.50	0.00	1.26	100.00	1.55	95.70
	moles	0.72	0.00	0.00	1.44	2.16	D					0.352	0.12	0.00	0.007	0.482		0.939
	m%	33.33	0.00	0.00	66.66	99.99						73.03	23.52	0.00	0.15	100.00		97.60
							84-5	1	1400 1350	77.48	91.69	95.69	13.87	0.00	0.44	100.00	3.44	98.397
												0.350	0.136	0.00	0.002	0.488		0.965
												71.72	27.87	0.00	0.41	100.00		98.99
							84-6	1	1400 1100	74.45	88.10	87.91	8.76	0.005	0.52	100.00	5.68	99.10
												0.359	0.086	0.00003	0.003	0.448		0.972
												80.13	19.20	0.007	0.67	100.00		99.50
							84-7	1	1400 1150	74.52	88.19	90.78	8.82	0.004	0.40	100.00	2.63	99.043
												0.370	0.087	0.00003	0.002	0.459		0.972
												80.61	18.95	0.007	0.44	100.00		99.48

A



TABLE III

Flux 101.96 Al <sub>2</sub> O <sub>3</sub>	Analysis 152.02 187.44 Cr <sub>2</sub> O <sub>3</sub> Ge <sub>2</sub> O <sub>3</sub>		Total	%Pb	Crystal Analyze			Total	Flux Wt loss		Crystal Yield		Comp Symbol	Remarks
	Al <sub>2</sub> O <sub>3</sub> (by diff)	Cr <sub>2</sub> O <sub>3</sub>			Ge <sub>2</sub> O <sub>3</sub>	gms	%		Th gms	Act gms				
14.96	0.003	0.00	100.00	18.17	99.316	0.184	0.00	100.00	23.1	5.4	9.56	0.32		
0.15	0.00002	0.00	0.497		0.979	0.0012	0.00	0.9802						
30.18	0.004	0.00	100.00		99.89	0.12	0.00	100.01						
11.80	0.003	0.00	100.00	4.58	99.893	0.107	0.00	100.00	56.7	13.3	23.06	24.0		
0.12	0.00002	0.00	0.480		0.980	0.0007	0.00	0.9807						
25.00	0.004	0.00	100.00		99.92	0.07	0.00	99.99						
Failed														
11.75	0.00	00.00	100.00	3.50	99.803	0.197	0.00	100.00	27.0	6.3	14.73	15.3		
0.13	0.00	0.00	0.482		0.979	0.0013	0.00	0.9803						
26.97	0.00	0.00	100.00		99.86	0.13	0.00	99.99						
11.64	0.00	00.00	100.00	2.05	99.865	0.135	0.00	100.00	51.2	12.0	23.74	25.9		
0.11	0.00	0.00	0.470		0.980	0.0009	0.00	0.9809						
23.40	0.00	0.00	100.00		99.90	0.09	0.00	99.99						
12.42														Incomplete solution
7.94	0.00	0.00	100.00	1.90	99.890	0.110	0.00	100.00	191.5	44.9	39.54	48.3		Cover opened
0.08	0.00	0.00	0.455		0.980	0.0007	0.00	0.9807						
17.58	0.00	0.00	100.00		99.92	0.07	0.00	99.99						
10.67	0.00	00.00	100.00	3.42	99.910	0.090	0.00	100.00	22.6	5.3	27.84	28.7		
0.11	0.00	0.00	0.474		0.980	0.0006	0.00	0.9806						
13.21	0.00	0.00	100.00		99.83	0.06	0.00	99.99						
10.47	0.00	00.00	100.00	1.37	99.905	0.095	0.00	100.00	45.4	10.6	28.74	33.0		
0.10	0.00	0.00	0.465		0.980	0.0006	0.00	0.9806						
11.51	0.00	0.00	100.00		99.83	0.06	0.00	99.99						Incomplete solution
Programmer malfunction														
8.40	0.016	0.00	100.00	6.76	99.912	0.058	0.00	100.000	8.77	2.0	37.55	37.54		
0.082	0.00030	0.00	0.455		0.980	0.0004	0.00	0.9804						
18.02	0.002	0.00	100.00		99.95	0.04	0.00	99.99						
14.56	0.004	0.00	100.00	2.71	99.770	0.230	0.00	100.00	17.07	4.0	11.26	5.30		
0.143	0.00003	0.00	0.491		0.979	0.0015	0.00	0.9805						
29.12	0.006	0.00	100.00		99.84	0.15	0.00	99.99						
10.43	0.00	0.00	100.00	5.29	100.00	0.00	0.00	100.00	57.02	13.4	28.85	31.05		No Cr added to melt
0.102	0.00	0.00	0.467		0.981	0.00	0.00	0.981						
21.84	0.00	0.00	100.00		100.00	0.00	0.00	100.00						
10.18	0.00	0.00	100.00	1.13	100.00	0.00	0.00	100.00	20.77	4.87	29.95	25.8		Oxygen added during run. No Cr
0.100	0.00	0.00	0.466		0.981	0.00	0.00	0.981						
21.46	0.00	0.00	100.00		100.00	0.00	0.00	100.00						Incomplete solution
9.60	0.00	0.00	100.00	1.13	99.892	0.108	0.00	100.00	48.97	11.48	32.12	31.4		O <sub>2</sub> + Cr
0.094	0.00	0.00	0.463		0.980	0.0007	0.00	0.9807						
20.30	0.00	0.00	100.00		99.82	0.07	0.00	99.99						
8.28	0.00	0.00	100.00	1.34	99.990	0.110	0.00	100.00	79.67	18.67	38.06	41.95		O <sub>2</sub> + Cr
0.081	0.00	0.00	0.455		0.980	0.0007	0.00	0.9807						
17.80	0.00	0.00	100.00		99.87	0.07	0.00	99.99						
14.69	0.00	0.49	100.00	4.71	98.38	0.00	1.62	100.00	22.07	5.5	19.71	14.1	A	
0.144	0.00	0.003	0.493		0.965	0.00	0.009	0.974						
29.21	0.00	0.61	100.00		99.07	0.00	0.92	99.99						
9.17	0.00	0.40	100.00	10.99	95.006	0.314	4.98	100.00	94.97	21.86	34.47	56.70	B	
0.069	0.00	0.002	0.419		0.932	0.0001	0.027	0.959						
21.24	0.00	0.48	100.00		97.18	0.01	2.81	100.00						
9.33	0.00	0.24	100.00	3.22	98.81	0.00	1.59	100.00	46.62	10.88	33.58	41.42	A	
0.092	0.00	0.001	0.462		0.965	0.00	0.009	0.974						
19.91	0.00	0.22	100.00		99.07	0.00	0.92	99.99						
12.50	0.00	1.26	100.00	1.55	95.70	0.00	4.30	100.00	130.07	29.94	20.05	25.8	B	
0.123	0.00	0.007	0.482		0.939	0.00	0.023	0.962						
25.52	0.00	0.15	100.00		97.60	0.00	2.39	99.99						
13.87	0.00	0.44	100.00	3.44	98.397	0.123	1.58	100.00	30.06	7.02	14.21	2.45	C	
0.136	0.00	0.002	0.488		0.965	0.0008	0.009	0.9748						
27.87	0.00	0.11	100.00		98.99	0.08	0.92	99.99						
8.76	0.005	0.52	100.00	5.68	99.10	0.120	0.78	100.00	31.54	7.36		32.0	C	
0.086	0.00003	0.003	0.448		0.972	0.0008	0.004	0.9768						
19.20	0.007	0.67	100.00		99.50	0.08	0.41	99.99						
8.82	0.004	0.40	100.00	2.63	99.043	0.157	0.80	100.00	11.54	2.69	35.75	25.8	C	
0.097	0.00003	0.002	0.459		0.972	0.0010	0.004	0.977						
18.95	0.007	0.44	100.00		99.48	0.10	0.41	99.99						

B

Run #	M. W. Units	Composition				Run #	Soak Time (hrs)	Temp °C		207.21 %Pb	245.21 Calc PbF <sub>2</sub>	245.21 by diff PbF <sub>2</sub>
		101.96 Al <sub>2</sub> O <sub>3</sub>	152.02 Cr <sub>2</sub> O <sub>3</sub>	187.44 Ga <sub>2</sub> O <sub>3</sub>	245.21 PbF <sub>2</sub>			Soak	Quench			
84						84-8	1	1400	1000	76.18	90.15	91.87
1-12												0.375
												82.78
						84-9	1	1400	1200	73.94	87.50	89.65
												0.366
												78.54
						84-10						
						84-11	1	1400	1350	78.42	92.80	84.64
												0.345
												69.56
						84-12	1	1400	1300	79.43	94.00	85.37
												0.348
												70.73
87	gms					87	1	1400	1000	81.17	96.06	92.08
	moles	See Table II										0.376
	m%											82.82

A

TABLE III (Continued)

07.21	245.21	245.21	101.96	Flux	Analysis			Crystal Analysis				Flt
				152.02	187.44		by diff.				wt	
Pb	Calc PbF <sub>2</sub>	by diff PbF <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	Ga <sub>2</sub> O <sub>3</sub>	Total	%Pb	Al <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	Ga <sub>2</sub> O <sub>3</sub>	Total	gms
6.18	90.15	91.87	7.75	0.009	0.38	100.00	5.07	99.780	0.220	0.30	100.00	183.
		0.375	0.076	0.00006	0.002	0.453		0.980	0.0015	0.003	0.985	
		82.78	16.78	0.013	0.44					0.31	99.95	
5.94	87.50	89.65	10.06	0.007	0.29	100.00	2.62	99.135	0.165	0.70	100.00	14.2
		0.366	0.100	0.00005	0.00	0.466		0.973	0.0011	0.004	0.9781	
		78.54	21.46	0.011	0.00	100.01		99.48	0.10	0.41	99.99	
4.42	92.80	84.64	15.36	0.00	0.00	100.00	2.90	100.00	0.00	0.00	100.00	27.7
		0.345	0.151	0.00	0.00	0.496		0.981	0.00	0.00	0.981	
		69.56	30.44	0.00	0.00	100.01		100.00	0.00	0.00	100.00	
4.43	94.00	85.37	14.63	0.00	0.00	100.00	2.58	100.00	0.00	0.00	100.00	59.
		0.348	0.144	0.00	0.00	0.491		0.981	0.00	0.00	0.981	
		70.73	29.27	0.00	0.00	100.00		100.00	0.00	0.00	100.00	
4.17	96.05	92.08	7.90	0.019	0.00	100.00	5.85	99.899	0.101	0.00	100.00	67.2
		0.376	0.078	0.00013	0.00	0.454		0.980	0.0007	0.00	0.9807	
		82.82	17.18	0.03	0.00	100.03		99.92	0.08	0.00	100.00	

<u>Crystal Analysis</u>				<u>Flux wt loss</u>		<u>Crystal Yield</u>		<u>Comp. Sym.</u>	<u>Remarks</u>
by diff. <u>Al<sub>2</sub>O<sub>3</sub></u>	<u>Cr<sub>2</sub>O<sub>3</sub></u>	<u>Ga<sub>2</sub>O<sub>3</sub></u>	<u>Total</u>	<u>gms</u>	<u>%</u>	<u>Th gms</u>	<u>Act gms</u>		
99.780	0.220	0.30	100.00	183.34	42.78	40.32	25.0	C	
0.980	0.0015	0.003	0.985						
		0.31	99.95						
99.135	0.165	0.70	100.00	14.24	3.32	30.46	23.4	C	
0.973	0.0011	0.004	0.9781						
99.48	0.10	0.41	99.99						
Not run									
100.00	0.00	0.00	100.00	27.75	6.51	7.85	5.4	D	
0.981	0.00	0.00	0.981						
100.00	0.00	0.00	100.00						
100.00	0.00	0.00	100.00	59.5	13.95	10.97	16.5	D	Crystals had small additional phase attached.
0.981	0.00	0.00	0.981						
100.00	0.00	0.00	100.00						
99.899	0.101	0.00	100.00	67.2	15.51	39.11	38.5		
0.980	0.0007	0.00	0.9807						
99.92	0.08	0.00	100.00						

### Experimental (Cont.)

method eliminates the problems of saturation of the melt at a given temperature and solvent evaporation and gave consistent results. In addition, analysis of the crystals permitted calculation of the Cr distribution coefficient at various temperatures.

As expected, values of  $\text{Al}_2\text{O}_3$  solubility using this technique were higher than those obtained when a method which did not involve stirring and cooling was used. Even after long soak periods, there was always the possibility of non-equilibrium conditions, because of slow solution rates. In addition, taking samples from the bottom of the crucible when complete solution did not occur gave poor results because it was impossible to separate the undissolved  $\text{Al}_2\text{O}_3$  from the dissolved  $\text{Al}_2\text{O}_3$  in the melt, (see runs No. 61 -- 67.) The curve for solubility of dilute ruby is shown in Figure 4 from values obtained in Runs, No. 68, 73 and 83.

### 3. Ruby vs. Sapphire Solubility in $\text{PbF}_2$

A comparison of the solubility data for ruby and sapphire shown in Figure 3 reveals that the addition of only 0.02 mole percent Cr reduced the solubility of pure sapphire. This conclusion is confirmed by data obtained by runs No. 65, 66, and 67, where identical runs with and without  $\text{Cr}_2\text{O}_3$  were quenched after soaking at a given temperature for 16 hours. In each case, a reduction of  $\text{Al}_2\text{O}_3$  solubility is detected with Cr present.

It will be observed that the solubility curve in Figure 4 is

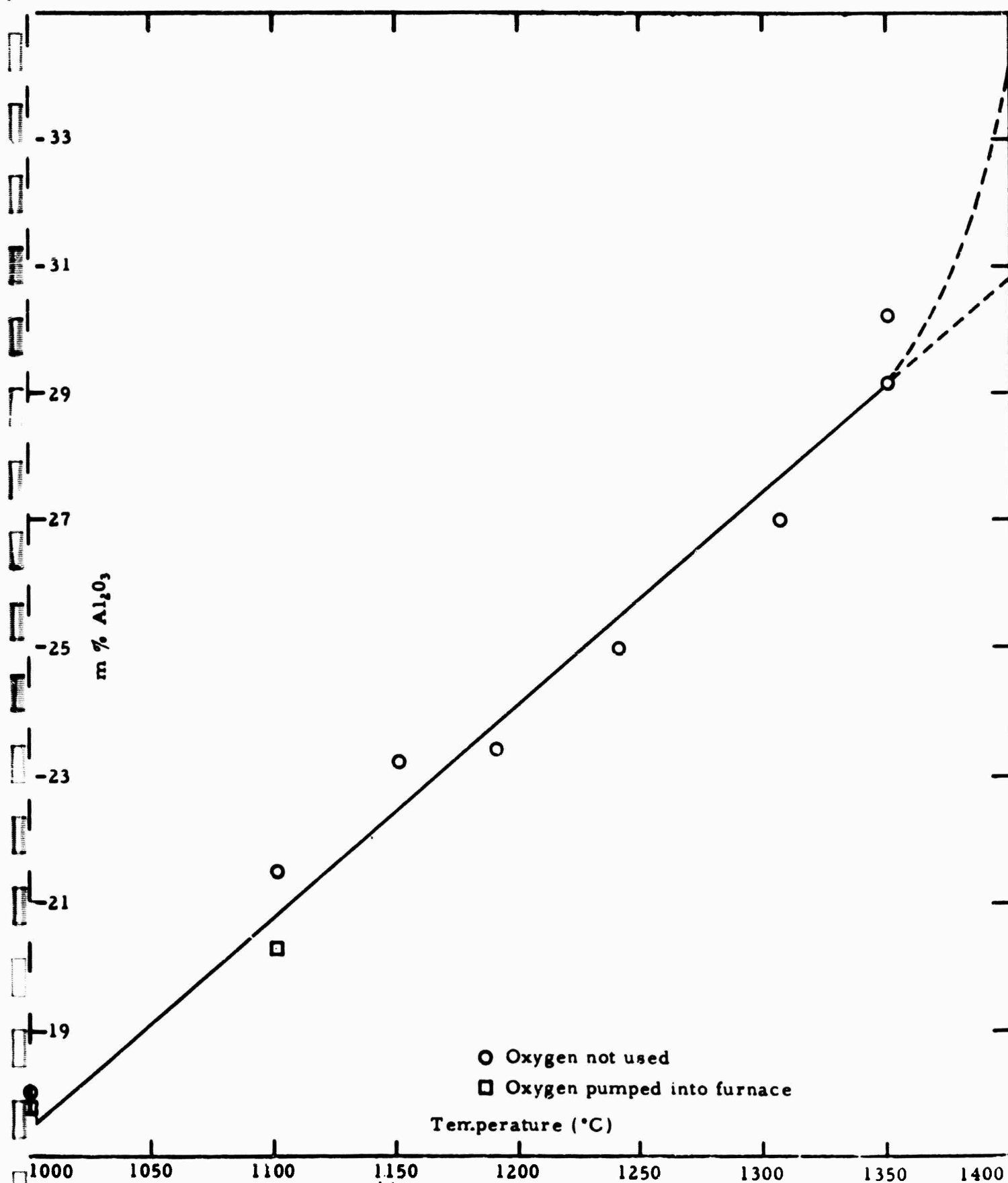


Figure 4  
Solubility of Dilute Ruby in  $\text{PbF}_2$

Experimental (Cont.)

drawn as a straight line. It can be seen, however, that an extension of this line would indicate only 30.7 mole percent  $\text{Al}_2\text{O}_3$  could be dissolved in  $\text{PbF}_2$  at  $1400^\circ\text{C}$ . Since 33 m percent is easily dissolved at  $1400^\circ\text{C}$ , a sharp upward curve probably takes place above  $1350^\circ\text{C}$  as indicated by the dotted line of Figure 4. In fact, if the lower points are joined in Figure 4, an upward curve is indicated above  $1300^\circ\text{C}$ . This would tend to confirm the belief that the initial crystallization of ruby is very rapid, even if no gross supersaturation occurs, with many thin plates crystallizing out over a very narrow temperature range. It is necessary, therefore, to cool very slowly in the  $1400 - 1350^\circ\text{C}$  range with very few temperature fluctuations, in order to prevent multiple nucleation from occurring in this temperature range. A large temperature gradient also helps to narrow the zone in which nucleation can occur, thus further reducing the amount of material which must crystallize at a given time.

4. Effect of Oxygen

There was some indication that oxygen pumped into the furnace increased the solubility of  $\text{Al}_2\text{O}_3$ . (Runs No. 83-5, 83-6, 83-8, and 83-9).  $\text{Al}_2\text{O}_3$  solubility with and without  $\text{O}_2$  was measured. In every case there was no detectable difference in solubility, see Figure 4.

5. Effect of Ga

The effect of Ga on sapphire and ruby solubility was determined in runs No. 84 (1-9). Compositions were made up in which 0.46 and 1.82 m

Experimental (Cont.)

percent Ga was added to a crucible containing  $\text{Al}_2\text{O}_3 + \text{PbF}_2$  but no  $\text{Cr}_2\text{O}_3$ ; and one in which both  $\text{Cr}_2\text{O}_3$  and  $\text{Ga}_2\text{O}_3$  were added. Solubility was reduced with increasing Ga concentration and the combination of both Ga and Cr further reduced the solubility of pure  $\text{Al}_2\text{O}_3$ . See Figure 5.

6. Distribution Coefficient

The apparent distribution coefficient of Cr in  $\text{Al}_2\text{O}_3$  crystals was measured by analyzing the total crystalline yield at each quench temperature from run No. 73. The sample from 73-1 which was quenched at  $1350^\circ\text{C}$  was quite small but the others offered sufficient samples for analysis. The results are shown in Table IV. It should be kept in mind that since the total yield at each quench temperature was sampled and analyzed, and since very little yield occurs at  $1350^\circ\text{C}$ , the actual distribution coefficient is much higher than is indicated by these figures. That is, the large yield of crystals at lower temperatures contains  $\text{Cr}^{3+}$  deposited over the entire temperature range. These results confirm our visual observation of a concentration gradient in all flux grown ruby such that the  $\text{Cr}^{3+}$  concentration decreases with temperature, see Figure 6a.

In the case of Ga, analysis of crystals from Run No. 84 indicates that no Ga concentration gradient exists. The two values for K at  $1350$  and  $1000^\circ\text{C}$  (Table IV) are open to question. The sample at  $1350^\circ\text{C}$  was quite small and since the percent Ga was such a small percentage the accuracy of the analysis is not good. At  $1000^\circ\text{C}$  two values for percent Ga were reported by the analyst, 6.94 and 0.38%. The wide divergence in these values would indicate some problem with sampling. There was insufficient time to repeat this analysis. The remaining three values all at  $K = 3.34$  for 6 samples quenched at  $1100^\circ\text{C}$  and  $1200^\circ\text{C}$  would indicate that no gradient exists for Ga in  $\text{Al}_2\text{O}_3$ . (See Figure 6b.)



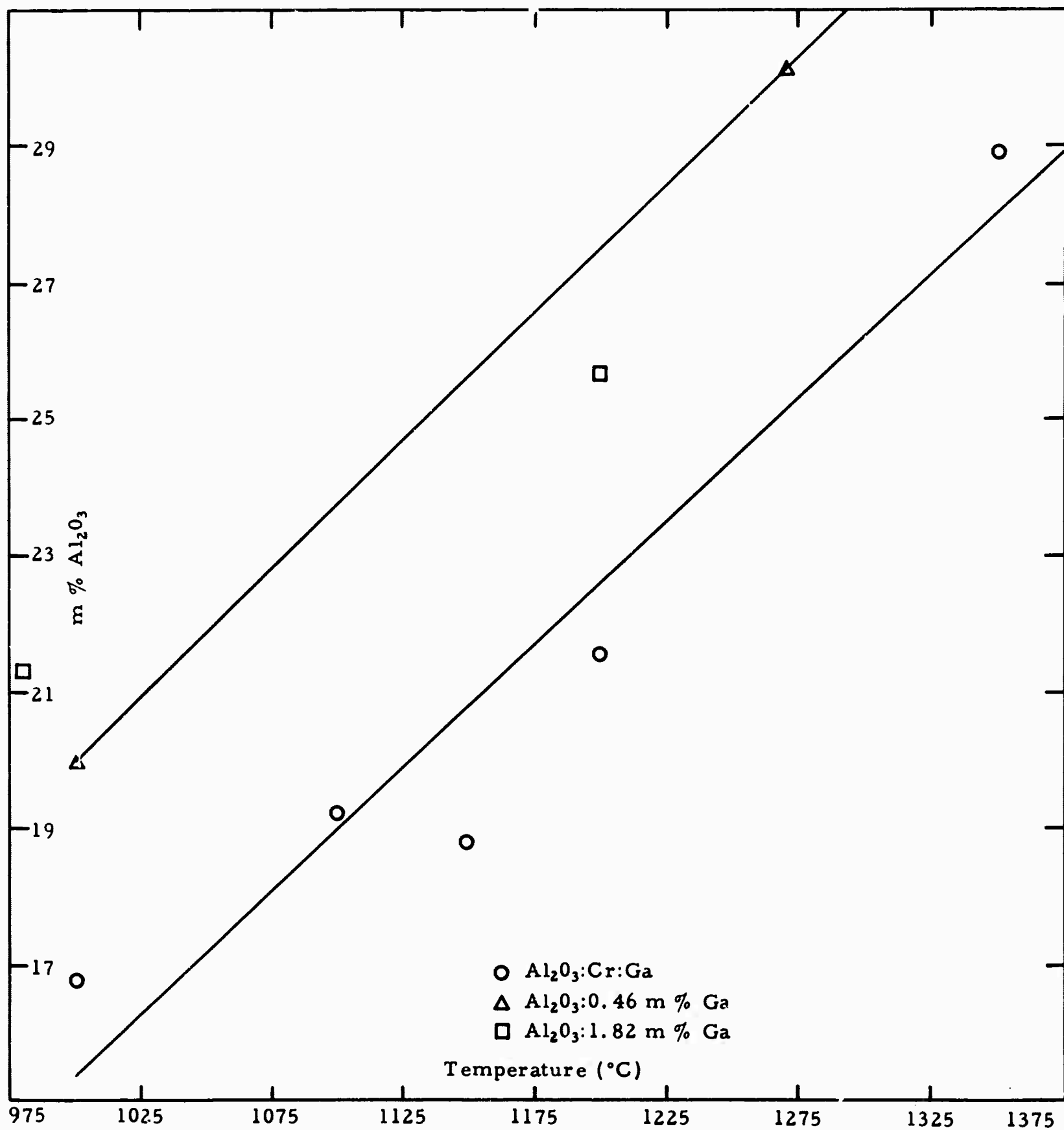


Figure 5  
Solubility of  $\text{Al}_2\text{O}_3$  with Ga and Cr Added

TABLE IV

<u>Temperature</u>	$K_{Cr} = \frac{\text{m \% Cr/Al}_2\text{O}_3 \text{ in melt}}{\text{m \% Cr in crystal}}$	$K_{Ga} = \frac{\text{m \% Ga/Al}_2\text{O}_3, \text{ Cr}_2\text{O}_3}{\text{m \% Ga in crystal}}$
1350°C	0.408	1.48
1311°C	0.419	----
1240°C	0.778	----
1200°C	----	3.35
1190°C	0.605	---
1150°C	0.908	3.34
1100°C	0.845	3.34
1000°C	0.972	4.49

Note also that in runs 84 (1 - 4), in which Ga but no Cr was added to  $\text{Al}_2\text{O}_3$ , samples quenched at 1270°C and 1000°C for one concentration of Ga, and 980°C and 1200°C for another, showed no significant change in percent Ga in the crystal samples analyzed.

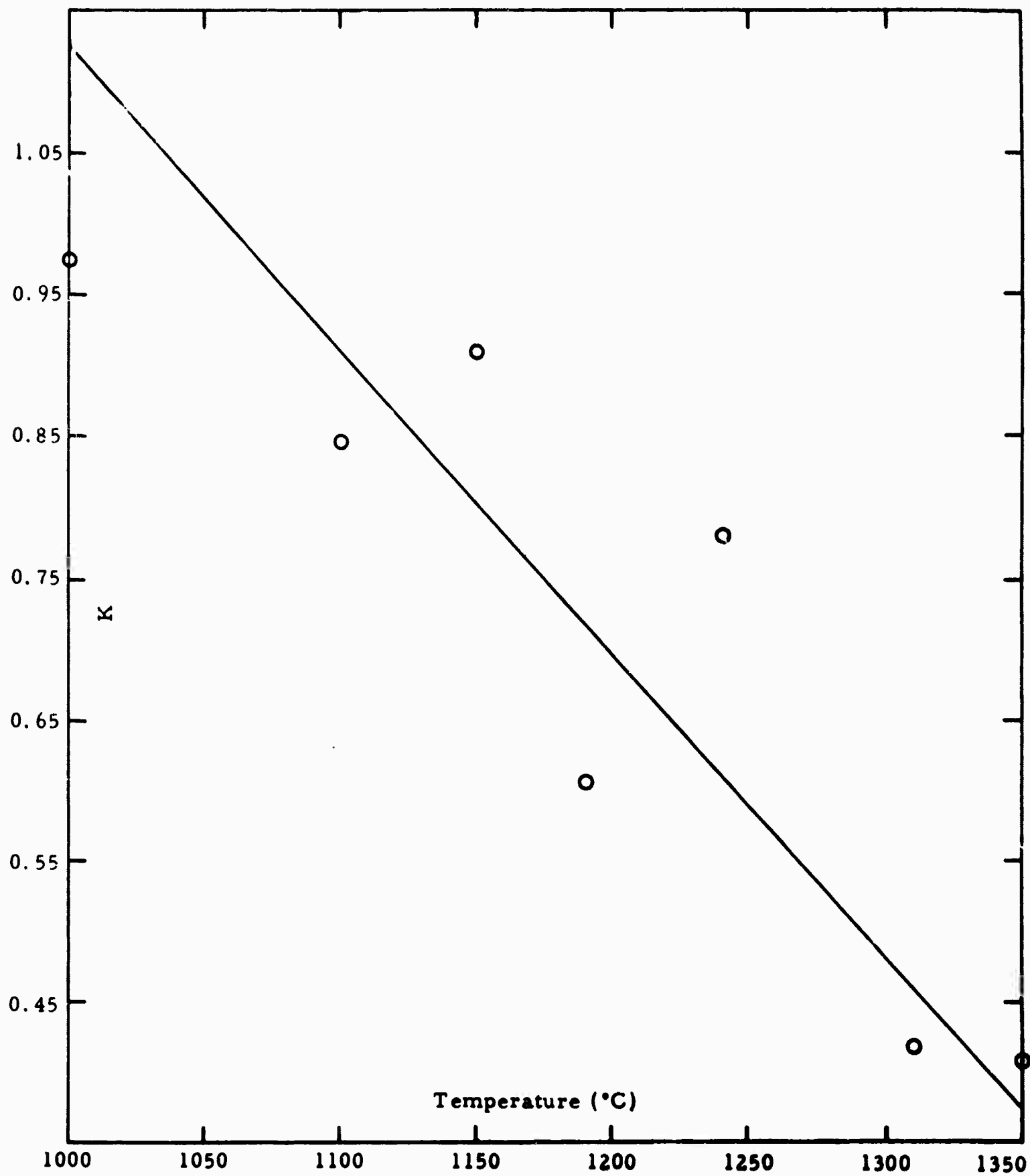


Figure 6a  
Distribution Coefficient of Cr in Al<sub>2</sub>O<sub>3</sub>

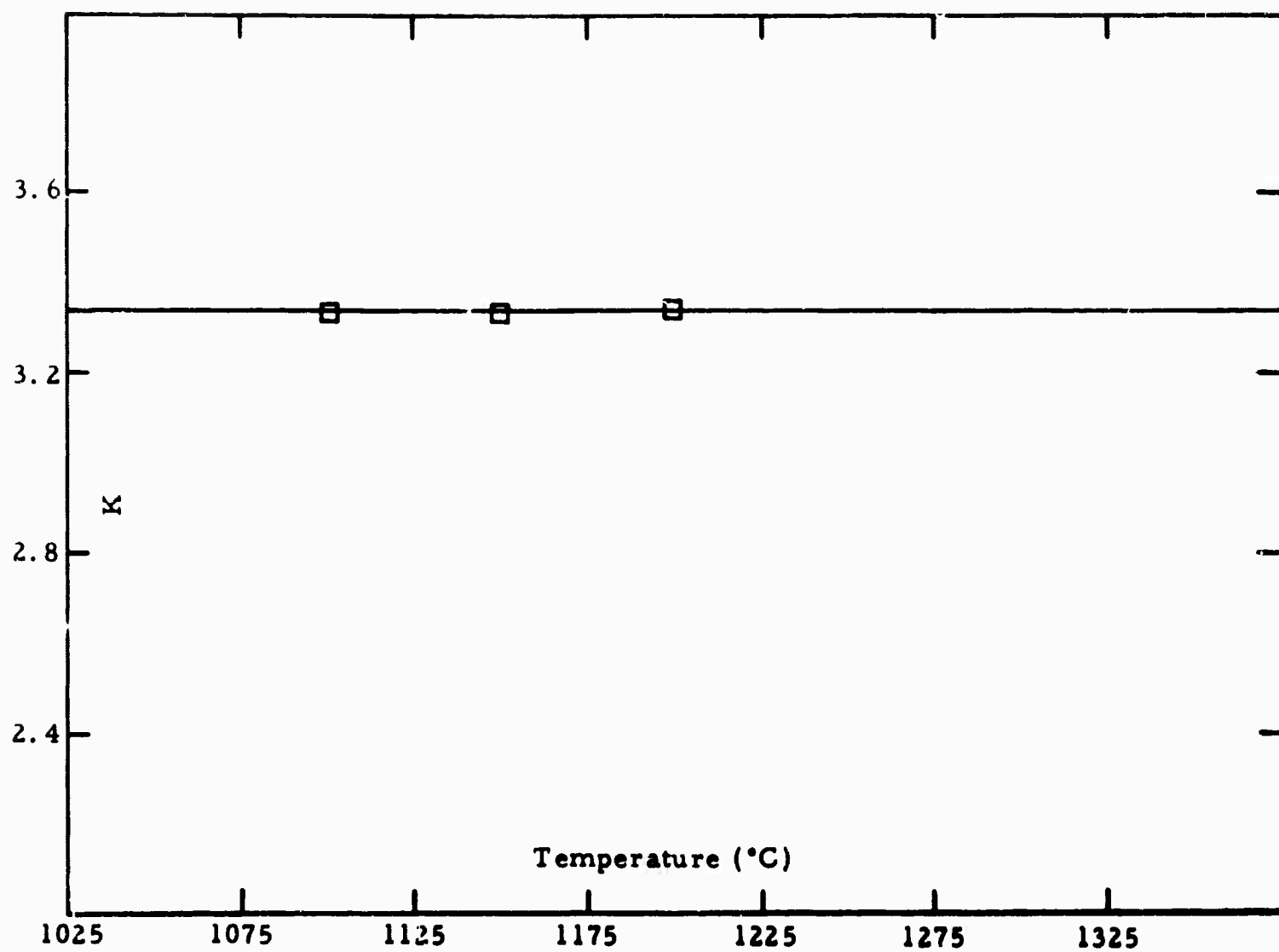


Figure 6b

Distribution Coefficient of Ga in  $\text{Al}_2\text{O}_3$

## Experimental (Cont.)

### C. Measurements

#### 1. Linewidth

Linewidth measurements were made on samples at the Litton Tube Division.

The crystals to be measured were immersed in liquid nitrogen in a quartz dewar. This equipment was placed in a box which permitted filtering of the exciting light as well as the fluorescent emission. A Dow Corning No. 4-76 filter was used for the incident beam and a No. 2-58 for the fluorescent beam. The exciting light was a high pressure mercury arc focused by an elliptical mirror. The sensing device was a Dumont K-2190(S20) photomultiplier. The light from the mercury arc was focused on the slit of the spectrograph. Both the entrance and exit slits were 20 microns wide. The linear reciprocal dispersion of the spectrograph was 5 Å per mm. The output of the phototube was amplified by a Vacuum Electronics Electrometer and the chart recordings were made on a Varian Chart Recorder.

Samples measured were numbers 26-1 and 26-2 (see Table II). These crystals were grown from a melt containing 0.27 and 1.34 m percent Ga respectively. Sample No. 13 contained no Ga and was used for comparative purposes. Table V is a summary of results, and Figure 7 is a curve of percent Ga vs.  $\Delta\lambda$ . The room temperature spectra of these samples compared to a Meller crystal are shown in Figure 8. The scale in the figure is 4.8 Å/mm. The spectra were taken at room temperature with

TABLE V

Sample No.	Description of Sample	Wavelength Linewidth		Remarks
		(A)	(cm <sup>-1</sup> )	
31	1/8" diameter ruby rod	6920	4.7	Small inclusions.
		6934	5.4	
Meller 60° orientation	Flame fusion ruby	6920	0.62	
		6934	1.0	
26-1	1 m percent Ga in ruby	6920	6.5	Flux inclusions.
		6934	7.2	
26-2	3 m percent Ga in ruby	6920	24.0	Flux inclusions.
		6934	18.1	
7	Ruby plates heavily doped	6920	6.0	Flux included plates.
		6934	8.0	
13	Ruby plates	6920	1.5	No flux inclusions.
		6934	1.8	
28-1	1 m percent Ga in ruby	6920	6.0	Flux Free.
		6934	7.6	
28-2	3 m percent Ga in ruby	6920	23.1	Small inclusions.
		6934	16.1	
31	Ruby plates	6920	3.5	Included.
		6934	4.1	
33	3 m percent Ga in ruby, very low Cr content.	6920	10.5	Flux free.
		6934	10.1	

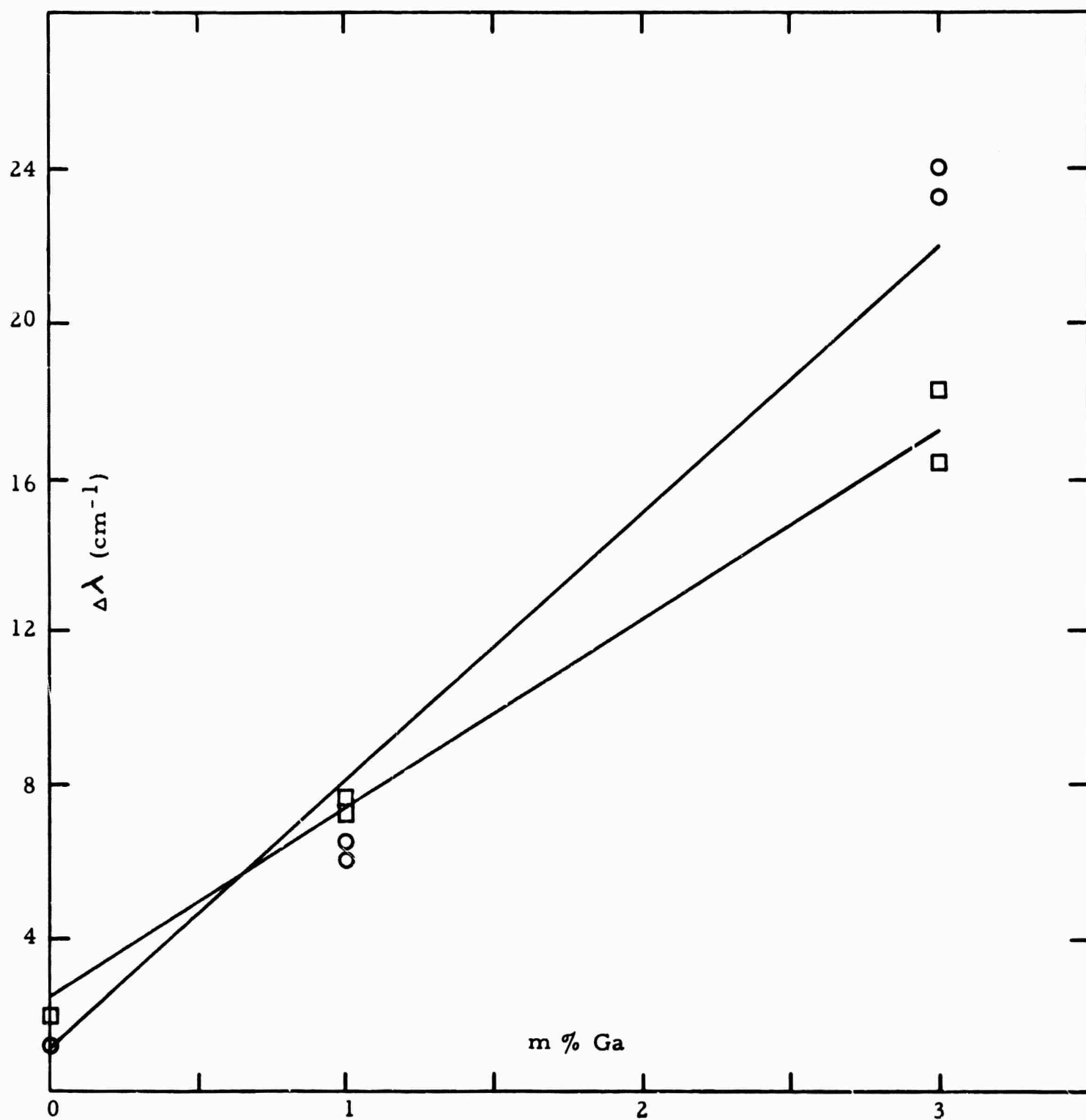


Figure 7

Percent Ga vs.  $\Delta\lambda$

Page 31

Airtron, a division of Litton Industries

Cobalt-60  
MILLER  
#1

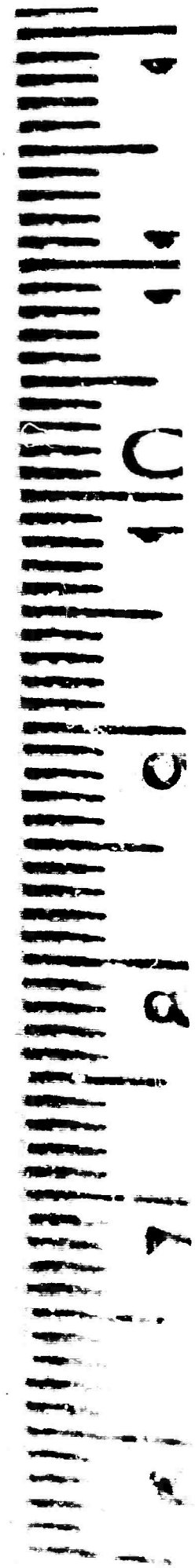


Figure 8 - Linewidth of Flux Grown Ga Doped Ruby Compared to a Meller Crystal at Room Temperature



Experimental (Cont.)

cobalt used as a standard. The samples were too heavily doped with chromium ( $\sim 0.2$  mole percent) and satellite lines are present. Measurements on other samples containing excessive chromium but no gallium have established that broadening observed in these samples is the result either of the high chromium content or concentration gradient. There is evidence that an optimum concentration of gallium as well as chromium exists and that for Ga it lies somewhere between 1 and 3 m percent. In the sample containing the higher gallium concentration, additional satellite lines show up suggesting the existence of pair states. The higher concentrations of Ga apparently no longer create a statistical distribution of crystalline fields around the  $\text{Cr}^{3+}$  ions; instead, discrete entities are set up having the same fields, which partly return the spectrum to the sharp line type, only much more complicated.

Some line broadening was present, however, in samples in which no Ga was added. Table VI shows data on additional linewidth measurements made. Ruby sample No. 70, which was of exceptionally high optical quality, had a linewidth about twice that of flame fusion ruby.

It was felt at first that the broadening was due only to the high Cr content and to the Cr concentration gradient. However, even when crystals with very low Cr concentrations were measured, or when very thin plates were used, a figure of about  $2 \text{ cm}^{-1}$  was obtained. It was obvious that with the very low strain present in these crystals, the cause of the residual broadening must be an impurity. We made a comparison of the flame fusion crystal with our flux grown crystal for trace impurities using spectrochemical analysis.

TABLE VI

	Linewidth (cm <sup>-1</sup> )		<u>Comments</u>
	<u>6934 (R<sub>1</sub>)</u>	<u>6920 (R<sub>2</sub>)</u>	
No. 70 Thin			.4 mm Thick
Edge	1.90	1.75	
Face	1.90	1.75	
No. 70 Thick			2.1 mm Thick
Edge	2.54	2.26	
Face	2.20	2.20	
No. 71 Thin			.4 mm Thick
Edge	2.20	1.90	
Face	2.10	1.96	
No. 71 Thick	2.10	2.0	Pyramidal all faces had about the same linewidth.
No. 73 - 122			
Edge	3.49	2.82	
No. 31 Rectangular			Gradient across
Rcd	4.1-5.75	3.9-5.15	face.
No. 56			
Face	4.74	4.32	
End	6.18	5.24	
No. 60			
End	4.74	4.0	
Face	3.19	2.88	
Flame Fusion	1.06	.87	

Experimental (Cont.)

The impurities found in samples No. 70 and 71 that were not present in the flame fusion crystals were approximately 0.001 percent iron and gallium. It is unlikely that these impurities are the cause of the broadening. It was decided that fluoride substitution for oxygen could be the cause of the broad linewidth. Fluoride substitution would lead to cation vacancies which would distort the crystalline field surrounding the  $\text{Cr}^{3+}$  ions.

In order to test this theory, two very carefully chosen pieces of ruby were polished and examined under 60 X magnification for any traces of included flux. None could be found. These samples, when analyzed spectroscopically, revealed 103 ppm fluorine, while lead was "not detectable, less than 30 ppm". This finding tends to confirm our theory of fluoride substitution.

2. Fluorescent Lifetime

Measurements of fluorescent lifetime were made at the Litton Tube Division by Mr. Michael Story. These measurements are important because an increase in linewidth should be accompanied by some decrease in lifetime. Measurements have indicated that in the 1 m percent sample only a small decrease in lifetime has occurred. At room temperature, a Meller ruby had a lifetime of 2.6 m sec. while the 1 m percent Ga sample had a lifetime of 2.2 m sec. and the 3 m percent sample had a lifetime of 1.6 m sec. Figure 9 shows a diagram of the apparatus used. The mercury arc was a Pek Labs. 109 high pressure mercury arc. The shutter was a rotating disk. The entrance slit, mirror, grating, and exit slit are all part of the Jarrell Ash 3.4 meter spectrograph. The photomultiplier was a red sensitive Dumont phototube and the oscilloscope was a Tektronic

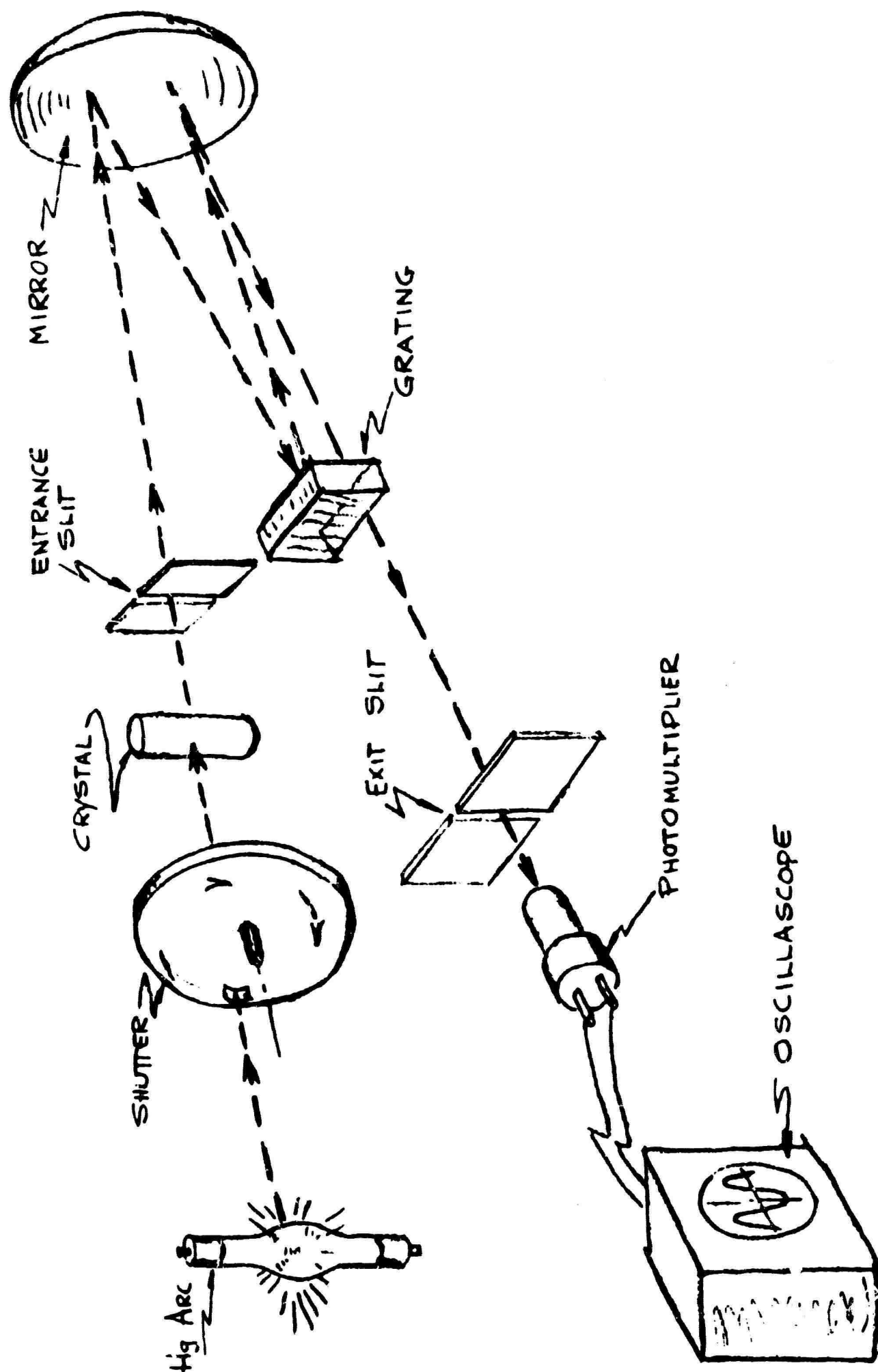


Figure 9 - Apparatus for Measuring Lifetime

Experimental (Cont.)

model 541A.

3. Laser Threshold

A plate from run No. 31 was cut into a rod about 0.1 x 0.1 x 1.4 inches. This cut rod revealed the rather sharp gradient which developed as the plate thickened. The rod was ground to a cylinder, polished and silvered. See figure 10. It was pumped with a G. E. Ft 524 lamp. After several attempts at lower levels, it lased at 2000 joules at 200°K. Another rod measuring 1.172 inches long x 0.213 inches in diameter, see Figure 11, was successfully lased in a 3 inch long laser head at 1200 joules at 200°K. The rod had several small flux inclusions which were not noticed until after it had been cut and polished. A concentration gradient was obvious when viewed on end. Furthermore, there is a defect visible in the photograph which resembles lineage.

D. Crystal Quality

The plates and rods produced in run number 31 were examined under crossed polaroids. Figure 12 compares the strain patterns of a plate of flux grown ruby with a plate of flame fusion ruby cut from an annealed, low strain flame fusion grown disc boule, viewed between crossed polaroids. There is a remarkable difference in the level of strain, the ruby plate being almost strain free. Figure 13 shows a rod of ruby under magnification viewed parallel to the plane of the plate from which it was cut. It can be seen that there is a complete absence of dopant irregularities. Note also that the concentration gradient does not appear to be uniform across the crystal, but is small across two-thirds, of the crystal and becomes sharp only across the last one-third.

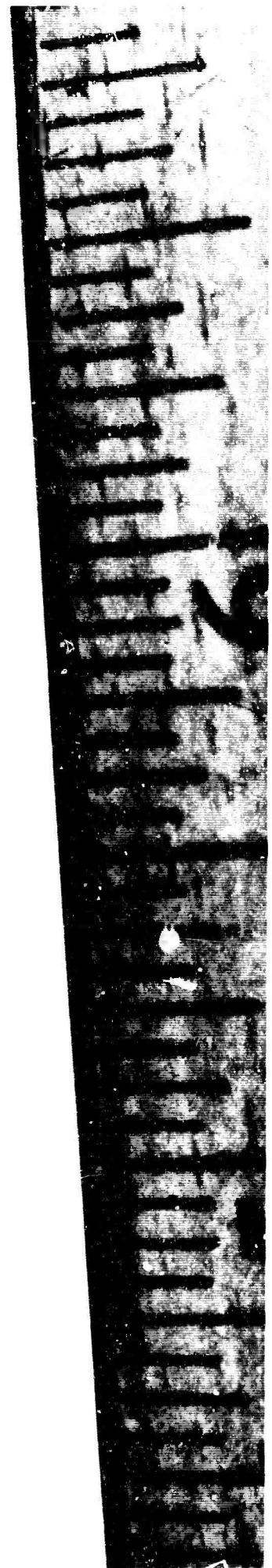


Figure 10 - Ruby Laser Rod

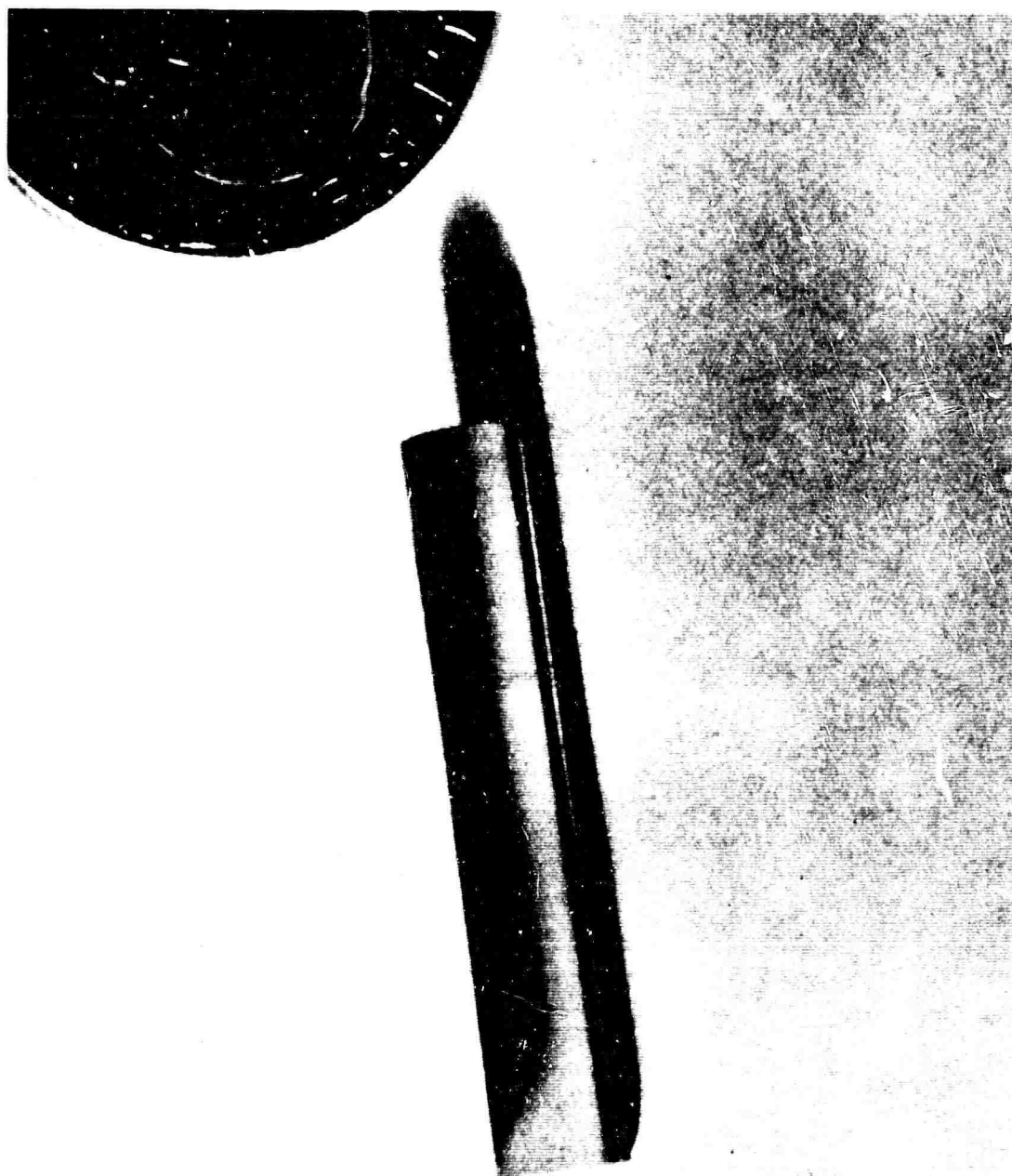


Figure 11 - Ruby Laser Rod



Figure 12  
Strain Pattern in Flame Fusion and Flux Grown Ruby  
Page 40



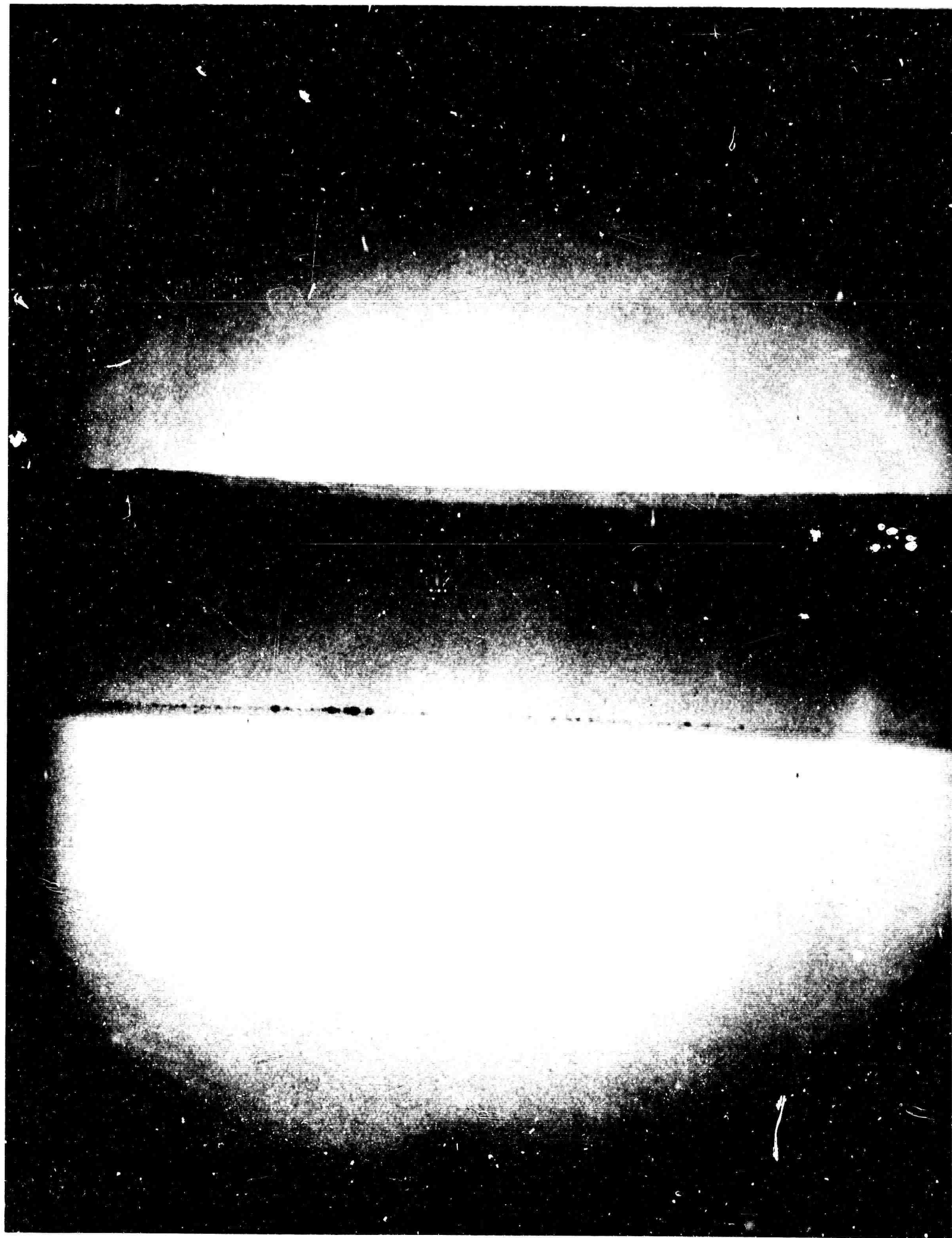


Figure 13  
Ruby Rod Magnified  
Page 41

Experimental (Cont.)

Crystals were cut and polished and then were observed under 350 times magnification for flaws and inclusions. In the thick plates grown under high gradients, no observable defects could be found. Small filaments were sometimes detected in polished plates.

Ruby crystal of high optical quality should not scatter a beam of light passing through it. When tested in our light scatter apparatus values only slighter higher than background could be detected.

Six samples of ruby, two of which were grown from flux at Airtron, the others flame fusion crystals, were examined at NRL.<sup>(5)</sup> The four types of tests performed were based on optic axis figure, shadow graphs, crossed polarizers and small angle scattering.

The optic axis figure measured the uniformity of direction of the optic axis. In this respect the Airtron ruby was rated "very good".

Evidence of abrupt discontinuities in chromium content called banding because of sharp circular bands of color was present in all flame fusion ruby samples but totally absent in flux grown samples. Gradations of color were present in all samples tested. However, flux crystals grown without cooling in run #86 showed no color gradations when examined microscopically. See Figure 14.

R. L. Barns, of the Bell Telephone Laboratories, Murray Hill, New Jersey, and W. J. Spencer of the Bell Telephone Laboratories, Allentown, Pennsylvania,



Figure 14

Ruby Crystal Grown on a Seed from Flux

Experimental (Cont.)

have examined two ruby plates grown under this program by the J. J. Lange technique. They have found that large regions appear to be dislocation free.\*

E. Analyses

A method of chemical analysis of Cr and Ga by x-ray fluorescence was perfected. The precision was quite good, but there was no way of knowing the accuracy, except by comparison with wet chemical analytical results, since no standards were available. Synthetic powder samples were made up. It appears that there is considerable divergence in Ga concentration in the ruby crystals reported by wet analysis and x-ray fluorescence. However, crystal quality of some of the sample was quite poor and part of the divergence can be blamed on poor sampling. The technique of x-ray fluorescence analysis is, of course, desirable for Ga and Cr detection, if it can be made as accurate as presently used wet analytical techniques. As soon as reliable standards are available, this should be the most convenient and reliable method.

\*We thank R. L. Barns for communicating these results prior to publication.

Experimental (Cont.)F. Equipment1. Temperature Measurements and Controla. Ten Inch I. D. Furnace

The furnace was an American Electric Company, model HTV-1023, modified by Research and Development Products Co. This furnace was heated by eight SiC heating elements wired as four parallel pairs across the two phase 208 volt secondary of a tap transformer. This furnace had some insulation changes from standard to improve the shell temperature. The standard insulation of these vertical tube furnaces called for two 4 1/2 inch courses of firebrick insulation. The inner or hotter of these was a 2600°F, 1425°C, firebrick. The outer of the two was a 2300°F, 1260°C, firebrick. The insulation was changed to two 3 1/2 inch courses plus an additional 2 inch course of high Q insulation. Aluminum foil was placed around the outside of the high Q insulation which was the 2 inch course. These changes reduced the furnace shell temperature

Experimental (Cont.)

to 70°C at the 1400°C operating temperature. In addition, these insulation changes should improve the operating efficiency of these furnaces.

The furnace had a ten inch inside diameter alumina core. The alumina cores for the furnaces were made of two different materials, Norton RA-98 and RA-139. We are presently using alumina cores manufactured by R & D Products Co. The crucible was a platinum can with straight sides and a garbage can type cover. This crucible held about 100 pounds of flux when fully loaded. This mass of material required the design of special equipment to handle the material and pour flux from the crystals.

Furnace life had always been a problem in molten salt crystal growth work. Furnace failures took place in several ways.

1. The furnace core was attacked by the vapor from the fluxes, especially fluoride vapors.
2. Furnace insulation was attacked by the same fluoride flux vapors.
3. Furnace insulation deteriorated through overheating.
4. The plugs and pedestals were attacked by either molten lead salts or vapors of these lead salts.

b. Loading, Unloading and Pouring Equipment

In the use of the large 10 inch furnace, it was necessary to handle large masses of material. This was done while the pedestal was at 1300°C during loading, or the loaded crucible was at 1000°C, before pouring. The total mass of crucible plus charge weighed about 100 pounds.

Experimental (Cont.)

This mass was impossible to handle by ordinary techniques. For this reason, a device was designed and built especially to do this job. This device had to be strong enough to support the weight and pour molten flux. It also had to be moved to a precise position with respect to the furnace pedestal. Its manipulation had to be simple. The loading or unloading of the furnace had to be accomplished in about 30 to 45 seconds after the pedestal had been lowered to its lowest position.

A new device was designed to do this job because nothing was available which would meet these requirements.

A clamshell type of holder was decided upon as the only convenient method of grasping the hot platinum crucible when approached from the front. The steel halves of the shell were lined with "Fiberfrax" insulation. The size was such that it held with a slight pressure the eight inch crucible; that is, about one-sixteenth of an inch less than eight inches i.d..

The opening of the halves was controlled by a lever attached to a nut on an Acme threaded rod. After one or two tries, this can be manipulated in 5 to 10 seconds to pick up the crucible or place it on the pedestal.

The device was designed to operate on angle iron tracks attached to channels in the floor.

Pouring took place by rotating a handle. Molten material was poured into a sand bath.

The device was manufactured by R & D Products Co. It was made

Experimental (Cont.)

of several pieces of pipe with extensions, tees, clamps, and heavy gauge material. This device appeared to work as expected. A photograph is shown in Figure 15.

The sequence of operations involved in unloading and pouring is shown in Figures 16 and 17. Figure 16 shows the pourer in position immediately after lowering the pedestal. Figure 17 shows the molten lead fluoride ( $\text{PbF}_2$ ) pouring into a platinum container in a sand bath.

Some of the problems encountered were:

1. Elevator drive.
2. Stirrer drive.
3. Pedestal design.
4. Thermocouple contact.

Possible methods considered for the elevator drive were an electric motor with a mechanical drive or a hydraulic pump. Space ruled out the hydraulic pump. The elevator drive (see figure 18) was by a 1/6 h. p. electric motor. A chain drive was used and four Acme threaded screws supported the table. A chain drive was selected because four screws must be driven together. The Acme lead screws were driven by rotating through bronze nuts attached to the steel



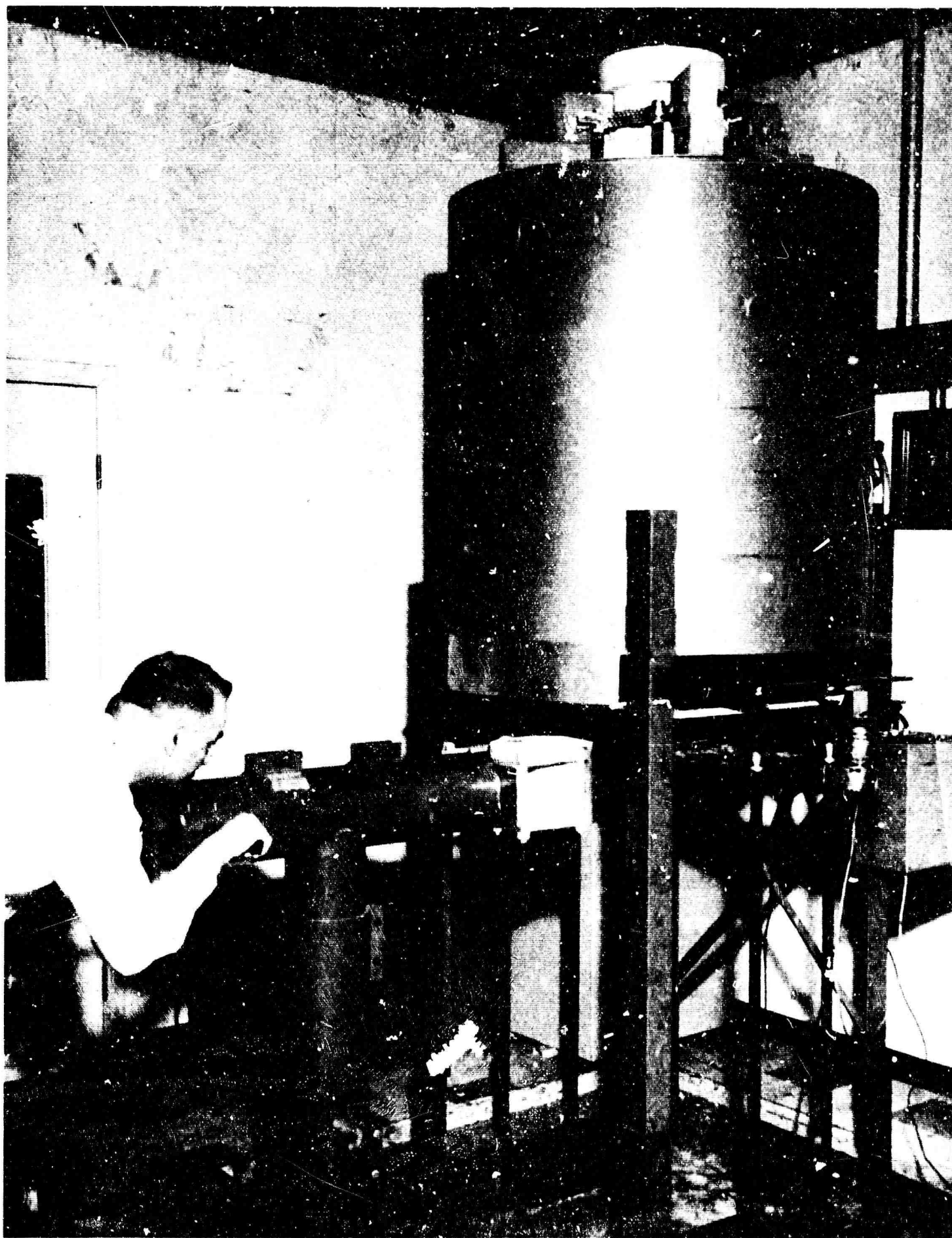


Figure 15  
American Electric Furnace  
Page 47



Figure 16 - Hot Crucible Leaving Furnace

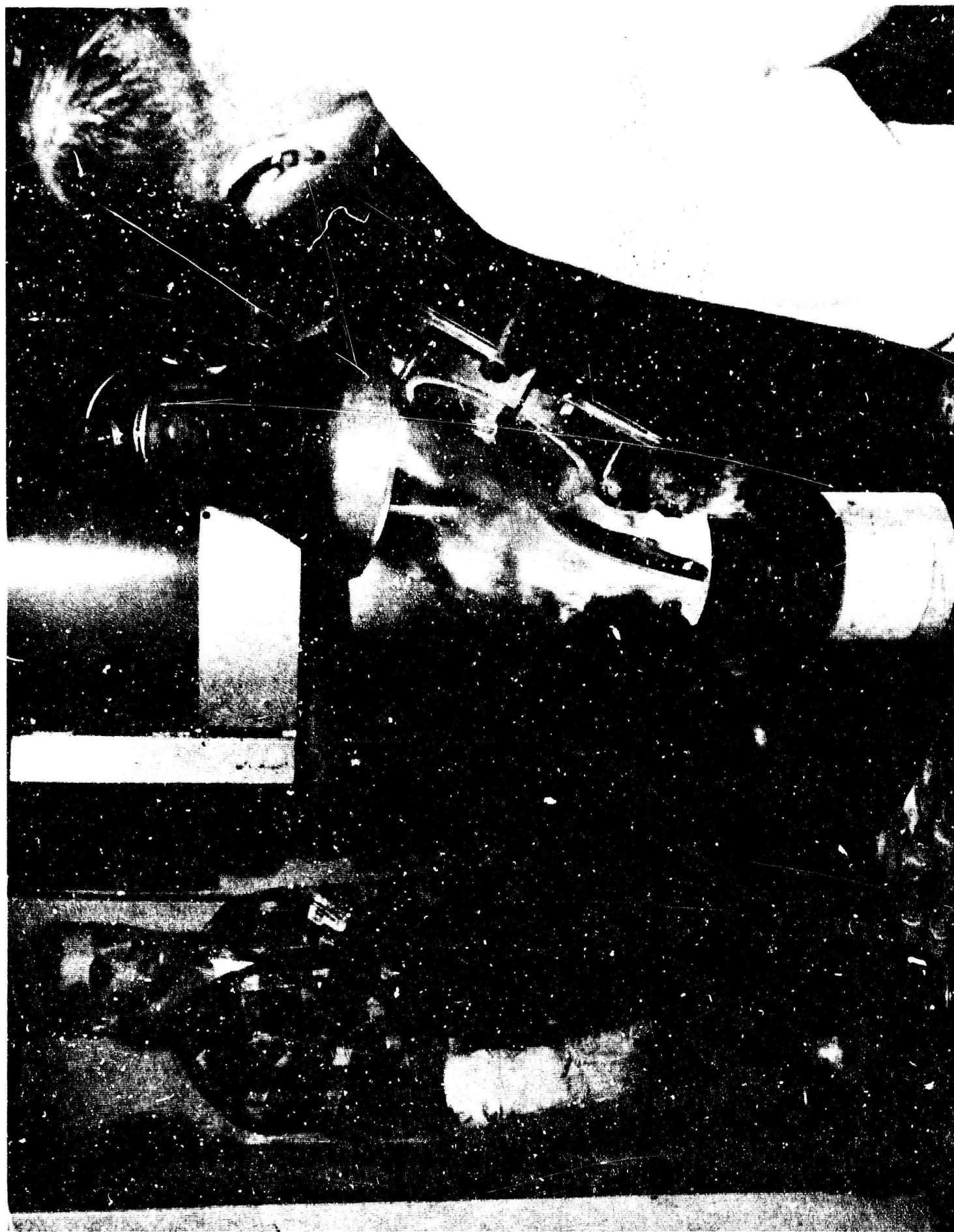


Figure 17 - Pouring of  $\text{PbF}_2$  Flux



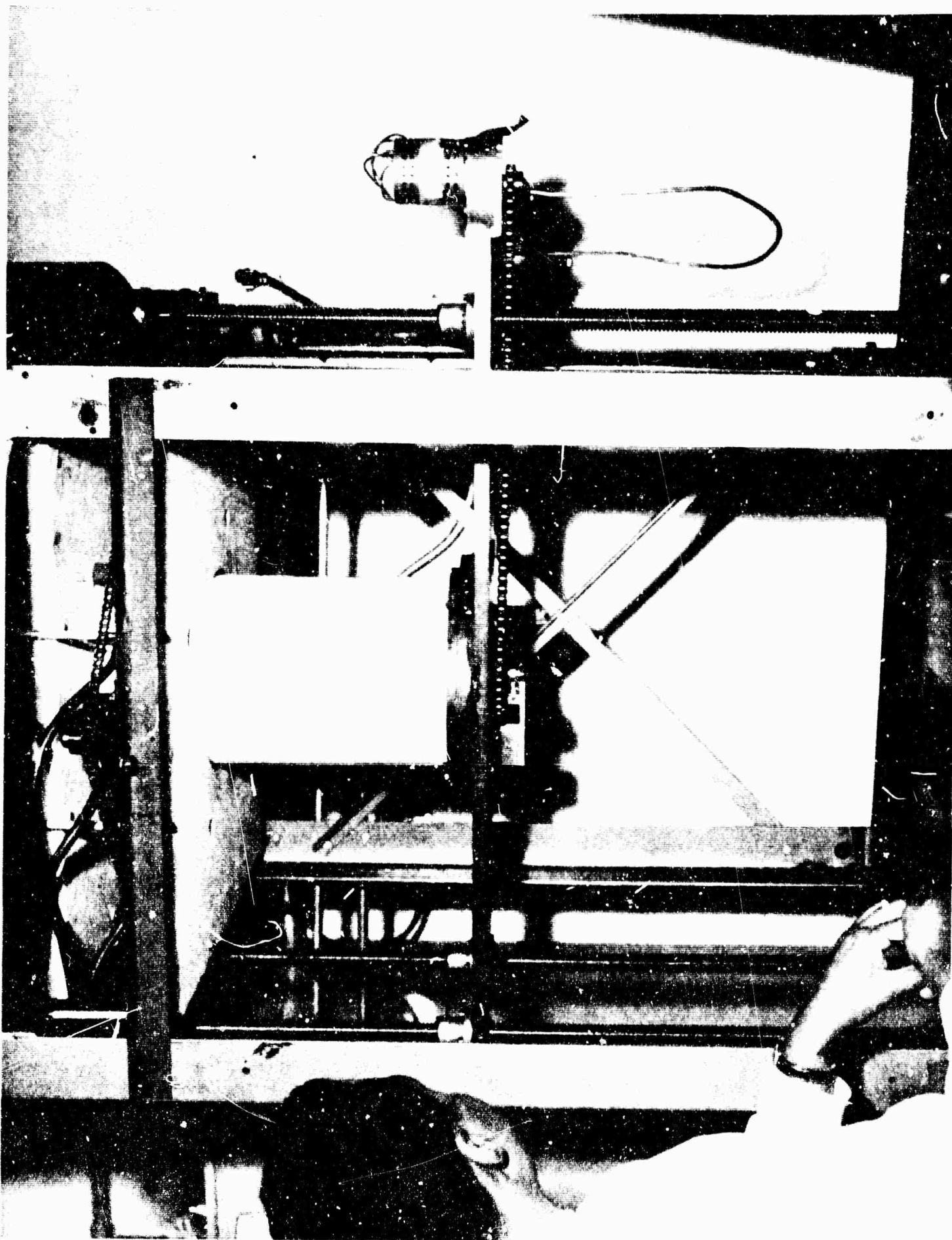


Figure 18 - Elevator Rotation Assembly

Experimental (Cont.)

table. Another important problem was where to place the drive motor. The possibilities were floor level, attached to the elevator table or at the top of the lead screws. Space demanded that the latter be chosen. The motor was mounted near the bottom of the furnace with the chain running around the outside with idler gears placed to keep the chain clear of the heating elements and under tension.

The elevator motors must, of course, be reversible. This could have been accomplished by interchanging two phases of a three phase motor or reversing a capacitor for a single phase motor. The three phase motor was preferable because it gave a positive reversal. It was possible using the single phase motor to reverse the switch without reversing the motor. It was necessary for rotation to stop completely before the single phase motor with two field windings could be reversed.

The stirrer drive problems included rotation of a load of more than 200 pounds. This was simplified by placing a turntable on a ball bearing raceway. This minimized friction losses. The necessary centering (the rotation must be about an extension of the furnace core axis) was accomplished by placing a drive shaft for the turntable in a bronze bearing on the elevator table. A chain drive was selected for space considerations. Reversal of rotation direction was necessary or the rotating crucible would quickly attain a state of mobile equilibrium. This would reduce stirring action considerably. Motor reversal took place in a similar manner to

Experimental (Cont.)

that for the elevator drive. There was one major difference. Using the stirrer required automation of this operation. This was done by using a synchronous motor to drive a cam which operated microswitches to drive the stirrer in one direction for 25 seconds, stop for 5 seconds, drive in the reverse direction for 25 seconds and stop for 5 seconds. These were for a one minute cycle. The microswitches functioned as a double pole-double throw switch with an off position. This either interchanged a capacitor between two pairs of field windings or interchanged two phases of a three phase motor.

Pedestals and top plugs had to be designed with load support, rotation, temperature measurement and crucible position in a furnace in mind.

Rotation required that the pedestal be perpendicular to the turntable, have true sides and top surfaces and move concentric with the furnace.

Temperature measurement was simple in the top plugs with thermocouple wells. These plugs were not rotated. The problem was considerably more difficult when rotation of a pedestal took place. It could be done, but only by using moving contacts. A set of slip rings with a lava insulator was used. This made several additional junctions because the thermocouple had to be attached to the slip rings. Contact was made to the slip rings and the contacts attached to the measuring

Experimental (Cont.)

circuit. Each of these contacts was potentially an uncompensated junction. The thermocouple (Pt vs. Pt 13 percent Rh) was soldered to the slip ring. Thermocouple lead wire was attached to the brushes.

The temperature was found to agree with an adjacent thermocouple within 5 degrees, the readability of the recorder, even though potential errors were present. This could be explained by the fact that the temperature was low (25°C or less) and the contacts created pairs of similar opposing junctions.

The plugs and pedestals were poured of a castable refractory (Norton 33HD) with a thermocouple well (high temperature alumina) in place. The molds used were finished to a close tolerance (out of round undetectable with a surface gauge). A steel plate with anchor pins was attached to the pedestal during casting. The steel plate was used with adjustable pins to position the pedestal on the turntable.

The length of the pedestal had to be tailored to the furnace. It dictated position of the crucible in the furnace. Pedestal length ideally had to be great enough to allow the crucible to be placed at any position in the furnace hot zone. It also had to be short enough to allow handling of the crucible for loading and unloading the furnace. These two requirements could be mutually exclusive. The sizes selected to optimize these as well as possible was 33 inches and 28 inches high.

Experimental (Cont.)

In early crystal growth runs in the ten inch furnace, there had been considerable nucleation on the walls of the crucible. The problem appeared to be cool walls of the platinum crucible.

The indications were that the furnace core was cooled abnormally. This probably was caused by a chimney effect. A draft of cold air went up through the annular space around the pedestal. As the furnace cooled, this cool air would cool the furnace walls and the crucible walls would be cooled by radiation or directly by the cold drafts blowing on the crucible walls. This problem was solved by an additional improvement which permitted the rotation and/or lowering of the pedestal to take place without cooling drafts to enter the furnace by the addition of flexible collar which was attached to the elevator and the underside of the furnace. See figure 19. When the pedestal was removed from the furnace rapidly to load or unload a charge, the collar was disconnected. The pedestal was free to rotate within the collar and could be slowly raised and lowered without disconnecting the collar. The collar was fitted with a nozzle to permit introduction of oxygen. This modification reduced nucleation on the walls of the platinum can which was caused by cold drafts entering around the periphery of the pedestal.

d. Temperature Controller

The temperature controller for the ten inch furnace is a unit designed and manufactured by Minneapolis-Honeywell. The control system consists of a Beck Controller, A Honeywell Temperature Set Point Unit.



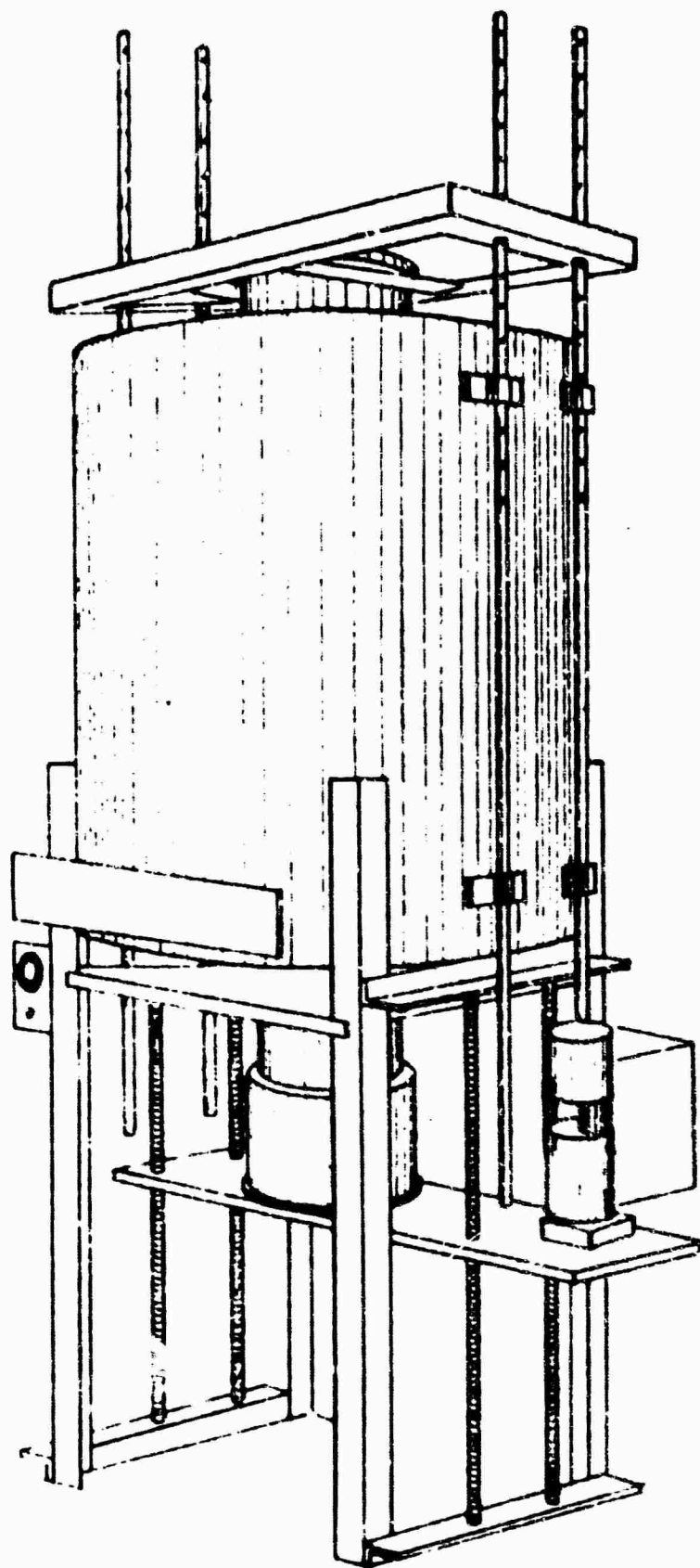


Figure 19  
Elevator and Collar Assembly

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Airtron, a division of Litton Industries

Experimental (Cont.)

Deviation Amplifier, Deviation Recorder, Electr-O-Volt 3 mode controller and a Magnetic Amplifier. In this equipment, the temperature set point unit selects a millivolt potential which is compared with the thermocouple output. The two signals, potentiometer and thermocouple, feed the two channels of a deviation amplifier. This unit puts out a signal proportional to the millivolt difference from zero or temperature difference from set point. The set point unit selects the potential by adjusting a ten turn potentiometer. This potentiometer has 537.9 turns per turn or a total of 5379 turns from end to end. Since the scale span is  $1600^{\circ}$ , the limit of resolution of this potentiometer is  $0.3^{\circ}\text{C}$ . This is also the limit of resolution of the equipment. The Deviation Amplifier takes the thermocouple signal and the Set Point signal and retaining the algebraic sign, amplifies the difference and sends an output signal to the Electr-O-Volt. The signal and its magnitude, length of time off, set point, and rate of approach to the set point all effect the output of this controller. The output signal of the controller goes to the magnetic amplifier which, in turn, controls the degree of saturation of the Saturable Core Reactor. The reactor controls the power input to the furnace.

This control unit operates on a three mode basis. The modes are: Proportional Band (a function of distance from Set Point); Rate (a function of rate of approach to the Set Point); and Reset (a function of the time the temperature has been off set point).

Experimental (Cont.)

The Beck Program Controller operates a soak from zero to sixty hours. At the end of the soak, a temperature program is initiated. The rate of cooling is controllable from 0.4 to 10 degrees per hour ( $\pm 0.1^{\circ}\text{C}$ ). The cooling rate is controlled by a synchronous motor drive on the ten turn potentiometer.

2. Crucible Attack

During the early part of this contract, crucible failure became very pronounced. In some instances, a brand new crucible failed within hours after having been placed in the furnace with a charge. Since each failure not only meant purchase of a new crucible, but often resulted in a spillage of  $\text{PbF}_2$  on the pedestal, plug, muffle and elements requiring replacement of these components as well, the solution of this problem was of paramount importance. A total of six failures directly attributable to the platinum crucible were experienced. After one failure, damage to the furnace was so extensive that even brick insulation had to be replaced.

Failures were usually of three types:

1. Extensive corrosion at the base of the platinum can.
2. Cracks, usually along the periphery of the base.
3. Extensive seepage of  $\text{Al}_2\text{O}_3$  through pin holes in the base and walls.

Experimental (Cont.)

Several experiments were tried to attempt to find the reason or cure for the attack. Since this attack seemed to occur only in the large 8 inch cans, a number of runs were made using the 250 ml crucible with premelting, with and without Cr. In each case crucibles in which premelting took place showed evidence of corrosion, brittleness and  $\text{Al}_2\text{O}_3$  seepage through the walls. Two innovations, a heavier bottom (0.050 inches in place of 0.030 inches) and a platinum liner accomplished little. While corrosion was reduced, seepage remained about the same and embrittlement actually increased. The problem was solved by the use of an oxygen flow into the furnace whenever the crucible was hot. This served to produce an oxygen rich atmosphere and completely stopped the Pt corrosion.

Most of the equipment which was designed for the large molten salt systems performed satisfactorily. Problems which arose and solutions used are summarized below:

<u>Problem</u>	<u>Solution</u>
1. Hollow SiC elements showed very much shorter lifetime than had been expected.	1. Purchased various kinds of silicon carbide heating elements from several manufacturers for test purposes.
2. Pt crucibles continue to be subject to chemical attack.	2. When a slow stream of oxygen was pumped into the furnace during the entire run including the premelting operation, no attack on the Pt crucible could be detected. After 6 months of operation, the Pt can is as good as new. This problem is completely solved by the use of oxygen.

Experimental (Cont.)

<u>Problem</u>	<u>Solution</u>
3. Cracking of pedestal and plugs. Expansion of pedestal at top causing it to bind in furnace.	3. Round all corners to reduce rapid heat loss. Reduce diameter of top portion of pedestal.

The primary requirement for good crystal growth is good temperature control. Inadequate temperature control is usually responsible for the small, badly formed, flux included crystals that make up the bulk of the yield of most molten salt crystal growth attempts. The primary function of the crystal growth equipment then is to provide good temperature control. It can be expected that as one problem of temperature control is solved, a second, which was perhaps masked by the first, will become apparent.

The first major problem encountered during this period was the inability of the Honeywell temperature control system to function properly. This equipment is rather complex and although it is capable of excellent control when it is functioning properly, any number of things can cause trouble before this condition is achieved. The two major aberrations which caused trouble did not occur continually, but were intermittent making detection and correction especially difficult. The trouble was finally found to be a defective potentiometer in one case and a bad voltage regulator tube in the other. When these parts were replaced with new ones, the equipment worked well, and there has been no recurrence of this problem.

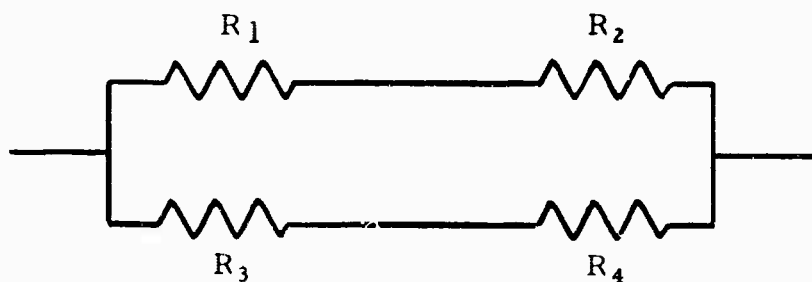
The next major problem was rapid and uneven aging of the SiC heating elements. The operating conditions are quite severe for these elements.

Experimental (Cont.)

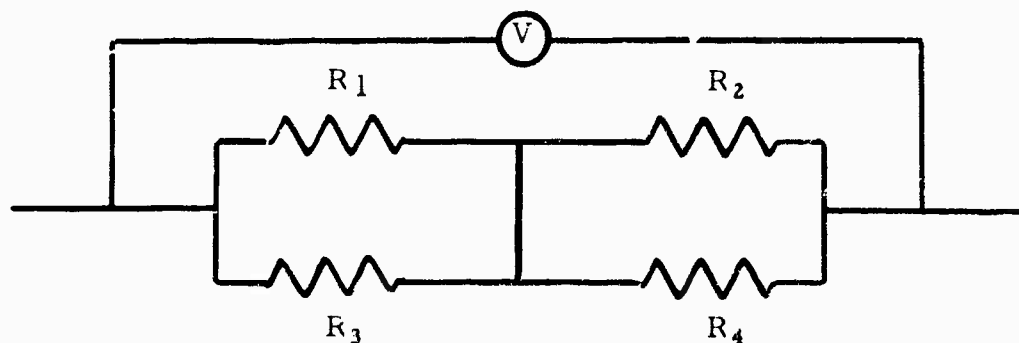
First, the present soak temperature of  $1400^{\circ}\text{C}$  at the pedestal requires a set point as high as  $1500^{\circ}\text{C}$ . Second, these temperatures must be maintained for long periods of time. At  $0.5^{\circ}\text{C}$  per hour cooling rate, twenty days are required to lower the temperature  $240^{\circ}\text{C}$ . Third, all holes must be tightly stuffed to prevent drafts which means that the elements must function in essentially a  $\text{PbF}_2$  atmosphere.

It is important that the elements age as little as possible and that they all age uniformly. This uniform aging is necessary because should one element increase in resistance more rapidly than another, or should one part of an element increase in resistance more rapidly than another, hot spots are created which adversely affect the crystal growth.

This problem was attacked in the following way: First, the series parallel network which looks like this:



was modified to look like this:



Experimental (Cont.)

This modification permits more even aging of the elements and facilitates the location of a bad element.

The ideal circuit would be one in which all of the elements operate on one circuit and all of the elements are in parallel. Each element would then tend to reach the same resistance and then age at the same rate.

With our present equipment, this can be achieved by substituting a 3 phase rectifier for the "3 phase to 2 phase" transformer plus a few wiring modifications. The difference in the voltage current relationship should be within the range of the reactor, the magnetic amplifier and the controller.

The next step was to order a number of different types of elements. These included high density "Globar" elements, solid "Hot Rods", and two types of spiral elements. None of these elements gave satisfactory performance except the spiral elements. These elements, manufactured by Morganite Inc. are very closely matched. They are one piece, hollow, high density recrystallized SiC, in which a spiral groove is cut. They are recommended by the manufacturer for operation at  $1450^{\circ}\text{C}$  -  $1700^{\circ}\text{C}$  where critical temperature uniformity and severe operating conditions are encountered.

The third modification was to rotate the crucible slowly after the soak period has ended. It will be recalled that during the soak period the pedestal is rotated for 55 seconds at 30 r.p.m. in one direction; at the end of which time it stops for 5 seconds; rotates in the opposite

Experimental (Cont.)

direction for 55 seconds; stops for 5 seconds, and then begins the cycle over again.

The reversing and pausing are achieved through two clock driven cams; one of which controls the time "on" and "off", the other controls the direction of rotation.

The rotational torque is supplied by a 3 phase "gear motor" with a 20:1 gear reduction to produce a 90 r.p.m. source of torque. At this point, an electromagnetic clutch is introduced. With a constant current flowing through its field, this device limits the maximum amount of torque that can be transmitted through it. The field current is adjusted so that no sudden start is made during the reversing operations. From the clutch, a chain drive, whose ratio is 3:1, transmits the torque to the pedestal which will now rotate at 30 r.p.m.

During the period of time that the furnace is cooling down and crystallization is taking place, it was thought that if the crucible could be rotated at a very slow speed, perhaps the effect on the crucible of one side of the furnace being cooler than the other could be eliminated.

To do this, a solenoid actuated dog clutch was used to mechanically connect the 90 r.p.m. output shaft of a second "gear motor" in tandem with the first motor which drives the pedestal continuously for the remaining portion of the run at 1.5 r.p.m.



Experimental (Cont.)

An additional modification which has been introduced in the 10 inch furnace is the use of an impervious muffle. The previous muffle used was a highly porous  $\text{Al}_2\text{O}_3$  body whose thermal shock resistance was not good. The porosity permitted a ready path for the  $\text{PbF}_2$  vapors to attack the heating elements and the large cracks which soon developed permitted the radiation from the elements to fall directly on the crucible. The new muffle of poured  $\text{Al}_2\text{O}_3$  which worked successfully is impervious and has excellent thermal shock resistance. It can be manufactured to much closer tolerances than the previous fired tube.

The firebrick walls of the furnace had been eroded away by the combination of heat and chemical attack. The walls of the furnace were chipped away for about one inch and replaced with a one inch poured alumina face. The alumina has a much higher resistance to  $\text{PbF}_2$  attack at the temperatures we are using.

## VII. CONCLUSIONS

The purpose of this work was to grow large, ruby crystals, from molten salt solutions. These crystals were to possess simultaneously high optical quality and broad spectral lines.

We have succeeded in deliberately broadening the emission linewidth of ruby through controlled gallium substitution, and many of the rubies grown have been free of strain and other defects. However, the size of the crystals obtained was not sufficient for large optical masers.

Other problems which were not completely solved, but for which solutions are indicated are:

### 1. C-Axis Growth

Ruby crystal growth from flux tends to be extremely anisotropic with little or no growth along the C-axis. Thus thin laminated plates are the usual type of crystal produced from molten salts, with large inclusions of solvent trapped between them. These inclusions are only partly due to the temperature fluctuations which are the major cause of single crystalline inclusions, but appear to result from the shape of the crystal growth as well.

It was found that ruby, crystallized under large temperature gradients, had a significantly greater C-axis growth resulting in thicker plates and fewer flux inclusions with no signs of laminations.

### 2. Flux Inclusions

It was found that while the thicker plates grew with fewer flux inclusions, there still is an undesirably large level of these imperfections. It

Conclusions (continued)

is felt that these inclusions result primarily from minor, localized, temperature fluctuations. The addition of a collar around the pedestal and careful stuffing of "K-O-Wool" around the top plug and core helps to reduce these fluctuations.

There is also some indication that the use of  $B_2O_3$  in the melt reduces the tendency to incorporate flux in the crystals.

3. Chromium Concentration Gradients

All the large crystals were grown by slowly cooling the melt. This resulted in a concentration gradient in Cr since its distribution coefficient is temperature dependent. The final part of the study was made using a static system containing excess ruby and a temperature difference imposed on the crucible. Crystals grown, although only a few grams in weight, were very uniform in Cr content. The solution to the problem of seeding the melts would fix this latter variable, as well as reduce the spurious nucleation which so severely limits the yield of usable material from these systems.

4. Linewidth

It was also found that rubies grown from  $PbF_2$  have larger than normal linewidths even without Ga substitution. This has been tentatively attributed to  $F^-$  substitution.

Conclusions (Cont.)5. Platinum Crucible corrosion

In order to maintain large platinum crucibles containing  $\text{PbF}_2$  -  $\text{Al}_2\text{O}_3$  melts at temperatures over  $1200^\circ\text{C}$  an oxygen atmosphere is required. The mechanism for the attack that occurs on crucibles heated in air is not understood.

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